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INTERNATIONAL GEOLOGICAL CONGRESS

REPORT OF THE EIGHTEENTH SESSION
GREAT BRITAIN 1948

PART II (2)

PROCEEDINGS OF SECTION A

PROBLEMS OF GEOCHEMISTRY

LONDON
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General Editor: A. J. Butler

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PROCEEDINGS OF SECTION A

PROBLEMS OF GEOCHEMISTRY

Edited by
C. E. TILLEY and S. R. NOCKOLDS

LONDON
1950

Section A, Problems of Geochemistry, met on three occasions during the Session. The successive Chairmen at these meetings were as follows :—

August 25th	Professor C. E. Tilley
	Professor P. Niggli
August 27th	Dr. N. L. Bowen
	Professor W. Wahl
August 30th	Dr. P. Geijer
	Professor D. S. Korzhinsky

Contents

SULL, ALTERABILITÀ DEI MINERALI DELLE ROCCE

Di CIRO ANDREATTA

Italy

ABSTRACT

I processi di alterazione dei minerali delle rocce si compendiano di solito in reazioni chimiche che mettono in rilievo l'idrolisi operata dalle acque circolanti. Tale modo di rappresentare l'alterazione non è esatto. E' necessario riferirsi sempre alla struttura cristallina dei minerali. Nel complesso edificio di particelle i diversi ioni hanno un comportamento in rapporto alle loro proprietà ed ai loro legami e polarizzazioni, ognuno con una propria individualità. L'acqua strappa dal reticolo cristallino diversi ioni in tempi successivi; in un lavoro precedente l'autore è arrivato alla conclusione che dal reticolo vengono allontanati ioni singoli o gruppi ionici in poliedri di coordinazione.

Il graduale allontanamento degli ioni positivi dall'edificio strutturale dei cristalli è posto dall'autore anche in rapporto con il potenziale di ionizzione degli elementi, per cui i primi ioni strappati da un reticolo dovrebbero essere quelli a più basso potenziale. Per i poliedri di coordinazione è molto più difficile schematizzare il comportamento. In base a queste ed altre considerazioni l'autore indica quali sono i fattori che determinano l'alterabilità dei minerali.

I PROBLEMI relativi all'alterazione dei minerali hanno offerto materia di frequenti ed ampie trattazioni in questi ultimi tempi, particolarmente in relazione con ricerche di grande attualità ed importanza quali sono gli studi di pedologia e sulle rocce argillose.

A mio modo di vedere, però, queste moderne ricerche sono state indirizzate e svolte quasi esclusivamente dal punto di vista chimico, passando così in sott'ordine la valutazione cristallochimica dei processi. Pur tenendo sempre nella dovuta considerazione la idrolisi operata dalle acque circolanti, cioè in definitiva l'azione di un componente del sistema sopra l'altro componente che è il minerale in via di alterazione, credo che non si debba trascurare l'azione esercitata dallo stesso minerale sopra lo svolgimento del processo. Il minerale non è soltanto una specie chimica, ma anche un aggregato spaziale di elementi, nel quale atomi, ioni e gruppi più complessi hanno tutti una loro individualità e inoltre sono strettamente interdipendenti in conseguenza delle reciproche attrazioni che li legano in un complesso edificio.

Secondo le vedute più recenti sull'argomento, l'alterazione dei minerali delle rocce, essenzialmente silicati, si svolge sopra la direttrice di una vera soluzione: l'acqua strappa dai reticoli cristallini ioni o gruppi di ioni in tanti stadi successivi, fino ad arrivare ad una completa distruzione del reticolo. Questo fatto si verifica in particolare nei processi naturali, nei quali l'acqua o le soluzioni circolanti si rinnovano continuamente, evitando che si stabilisca un equilibrio del sistema che interrompa il processo stesso.

In un recente lavoro (Andreatta, 1948) ho messo in risalto queste moderne vedute sull'alterazione dei minerali; a tale lavoro rimando per la principale bibliografia in proposito. Qui mi limito a ricordare una conclusione che ho tratto circa le modalità con le quali si esplica l'alterazione: mentre i metalli alcalini e alcalino-terrosi vengono strappati gradualmente dal reticolo cristallino come ioni, Si ed Al, e parzialmente forse anche Fe, vengono asportati in aggruppamenti con O e OH aventi il carattere e l'individualità di poliedri di coordinazione tetraedrici e ottaedrici. Secondo il mio punto di vista, il Si dovrebbe passare in soluzione sotto forma di tetraedri SiO_4 liberi o variamente legati fra di loro con le modalità note per i silicati, dato che è stato sperimentalmente accertato che nelle soluzioni di alterazione sono presenti radicali di diversi acidi silicici. Invece l'Al dovrebbe formare poliedri di coordinazione AlX_6 (dove X è O oppure OH), legati fra di loro in modo da dare frammenti di reticoli aventi forma lamellare (" micelle laminari "). Questi frammenti laminari formerebbero i

germi per la costituzione dei reticoli stratificati dei minerali che prendono origine dalle sostanze portate in soluzione durante l'alterazione (minerali argillosi in senso lato e idrati di Al e di Fe).

Questo semplice accenno ad una conclusione del lavoro citato fa comprendere come io abbia voluto tenere in considerazione, non l'elemento isolato ma l'elemento legato, in un edificio cristallino, ad altri elementi più o meno strettamente, all'opposto di quanto è fatto nella maggior parte delle moderne trattazioni sull'alterazione dei minerali e delle rocce. A questo proposito ricordo l'interessante rassegna dei processi di alterazione, dal punto di vista chimico e geologico, compendiata in un recente lavoro (Reiche, 1945), che comprende anche una ricca citazione bibliografica.

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Indirizzando la trattazione dei processi di alterazione dei minerali delle rocce sopra l'esame del comportamento dei reticoli cristallini durante l'alterazione stessa, si arriva spontaneamente al tentativo di ricercare ed individuare gli argomenti che diano spiegazione del grado di alterabilità dei minerali. In altre parole, ho tentato di rispondere a queste domande: perchè da un reticolo cristallino vengono rimossi diversi elementi in tempi successivi? Perchè alcuni minerali si alterano prima ed altri dopo in uno stesso processo? E' evidente che se si trovano esaurienti risposte a queste domande si può arrivare facilmente a compilare in base a dati precisi una scala delle alterabilità dei minerali, indipendentemente dai risultati ottenuti dalla pratica sperimentazione.

A questo scopo ho iniziato una serie di studi che mi hanno convinto delle enormi difficoltà che esistono per la preparazione di una scala teorica dell'alterabilità.

Il presente lavoro ha lo scopo di notificare alcune mie considerazioni in proposito e perciò non può essere conclusivo. Spero di poter portare a soluzione l'interessante problema in un tempo successivo, dopo aver raccolto una grande massa di risultati sperimentali che permettano di controllare punto per punto le mie deduzioni teoriche.

*   *   *   *   *

L'allontanamento degli ioni positivi dai reticoli cristallini dei minerali dovrebbe essere anzitutto in rapporto coll'*energia di ionizzazione* dei singoli elementi e con i legami che trattengono tali elementi nel reticolo cristallino, cioè con la loro *valenza elettrostatica*, per le sostanze aventi reticoli ionici. E' noto che fra i composti più solubili sono quelli dei metalli alcalini, come è altrettanto noto che nella maggioranza dei casi gli atomi alcalini sono i primi che si allontanano da un reticolo a costituzione complessa. Orbene i metalli alcalini sono proprio gli elementi che presentano i minimi valori di energia di ionizzazione. Infatti, per estrazione del primo elettrone, cioè per trasformare l'elemento in ione positivo monovalente, occorre un potenziale in volts di 3,87 per Cs, 4,16 per Rb, 4,32 per K, 5,11 per Na e 5,36 per Li. Si noti in particolare che la rimozione di un elemento da un reticolo cristallino, nel senso chimico dell'idrolisi, corrisponde proprio alla sua trasformazione in ione.

Seguono, in ordine di solubilità dei loro composti e di facilità di allontanamento da un reticolo cristallino, i metalli bivalenti alcalino-terrosi, che presentano energie di ionizzazione notevolmente più alte di quelle dei metalli alcalini, dato anche che essi si devono allontanare come ioni positivi bivalenti. La stessa intensità dei legami, che è maggiore per tali elementi bivalenti rispetto a quelli monovalenti, si oppone più fortemente alla rimozione dal reticolo cristallino essenzialmente in base alle stesse ragioni fisiche.

Quando infine consideriamo elementi trivalenti e tetravalenti, che possiedono ancor più alti valori di energia di ionizzazione, siamo indotti ad ammettere che la semplice azione idrolitica delle acque circolanti non riesca più a staccarli dagli altri elementi del reticolo cristallino direttamente collegati con essi. Ho già in precedenza illustrato il mio parere riguardo all'allontanamento di Al e di Si dai reticoli cristallini, che dovrebbero staccarsi in forma di poliedri di coordinazione. Per tali aggruppamenti è evidente che non si può parlare di energia di ionizzazione: siccome all'esterno di questi gruppi di coordinazione vengono a trovarsi ioni di O, si potrà se mai parlare di affinità elettronica di questi atomi.

Nei minerali a composizione molto semplice credo sia facile calcolare senz'altro l'alterabilità in base alle energie di ionizzazione degli atomi metallici. Ma formare una scala di alterabilità solo riferendosi a questi valori non è stato possibile, perchè ho dovuto constatare che l'alterabilità dei minerali, e perciò la stabilità di fronte all'alterazione, dipende da diversi altri fattori.

Oltre alla bassa energia di ionizzazione ed ai deboli legami nel reticolo, ritengo siano fattori di alterabilità anche condizioni puramente cristallochimiche, soprattutto le modalità di aggregazione degli elementi. Così, per esempio, la presenza di *tetraedri di coordinazione* AlO_4 è, secondo me, fattore di instabilità. Già ho dimostrato nel lavoro citato in precedenza, che il tetraedro AlO_4 non è fra i più stabili, dati i rapporti fra i raggi ionici dei componenti; tale tetraedro tende a trasformarsi in ottaedro AlX_6 (dove X sia O oppure OH).

In base a questa conclusione gli allumosilicati verrebbero ad essere più alterabili dei corrispondenti termini non alluminiferi e tanto più alterabili quanto maggiore è il contenuto di gruppi AlO_4. In realtà è stato stabilito che nefelina e leucite sono fra i silicati più facilmente alterabili e che fra i feldispati i più stabili di fronte all'alterazione sono i termini alcalini puri, mentre l'anortite è abbastanza facilmente alterabile.

In senso completamente opposto dovrebbero far sentire la propria influenza i *tetraedri di coordinazione* SiO_4, l'abbondanza dei quali dovrebbe rappresentare un elemento di stabilità di fronte all'alterazione. Nello stesso senso, e per le stesse ragioni, devono agire i legami più o meno abbondanti fra i tetraedri. Dunque in linea generale si dovrebbe notare una diminuzione di alterabilità passando dai silicati a tetraedri isolati (nesosilicati), a quelli a gruppi (sorosilicati), ai silicati a catene (inosilicati) ed a strati di tetraedri (fillosilicati), fino a raggiungere il massimo di stabilità nei tettosilicati, come per esempio nel quarzo, scarsamente alterabile e solubile. Naturalmente si deve sempre tener presente l'influenza positiva o negativa degli altri fattori, che possono spiegare la maggior parte delle eccezioni. Così la presenza nel reticolo cristallino di poliedri di coordinazione molto stabili di fronte ai processi di alterazione, rende poco alterabili alcuni nesosilicati e sorosilicati, come la presenza di poliedri poco stabili (per esempio AlO_4) rende instabili diversi tettosilicati.

Poliedri di coordinazione che abbassano l'alterabilità di molti silicati ritengo siano gli *ottaedri AlX_6 ed altri analoghi poliedri a grande stabilità* (TiO_6, ZrO_6, ecc.). Così si spiegherebbe la scarsa alterabilità dei granati, nel reticolo dei quali esistono poliedri AlO_6 oppure $Fe'''O_6$, dello zircone che contiene gli ottaedri ZrO_6, del rutilo che contiene ottaedri TiO_6, della cianite che possiede pure gli AlO_6, ecc.; mentre questi minerali per la presenza di pochi tetraedri SiO_4 non dovrebbero essere molto stabili.

Il concetto dell'influenza della quantità di tetraedri SiO_4 sopra la alterabilità dei silicati è già stato implicitamente accettato (vedasi anche il riassuntivo citato lavoro di Reiche), ma è stato espresso diversamente, cioè sempre con senso chimico. Infatti in tutti i trattati della materia si può leggere che l'alterabilità dei silicati aumenta quanto più questi minerali sono " basici," cioè ricchi di ossidi metallici e poveri di SiO_2 (olivina, anortite, ecc.). Questo concetto in definitiva concorda anche con la mia conclusione prima enunciata, essere cioè l'alterabilità dei silicati tanto maggiore quanto più alto è il contenuto in metalli monovalenti e bivalenti, a bassa energia di ionizzazione.

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Da questi brevi cenni si può genericamente dedurre che, secondo l'autore, l'alterabilità dei minerali delle rocce, riferita al reticolo cristallino, dipende essenzialmente da questi tre fattori:

(1) L'energia di ionizzazione degli elementi metallici facenti parte del reticolo cristallino e l'abbondanza degli stessi elementi.

(2) La stabilità dei poliedri di coordinazione degli elementi a più alta valenza, stabilità che si deduce dai rapporti dei raggi ionici dei componenti.

(3) L'abbondanza relativa dei tetraedri SiO_4 ed il numero dei legami fra gli stessi tetraedri e in generale il motivo strutturale col quale sono collegati nello spazio i diversi poliedri di coordinazione.

Nessuna relazione ho potuto trovare fra l'alterabilità dei minerali delle rocce e l'addensamento delle particelle nel reticolo cristallino nel senso del " packing index " (Fairbairn, 1943).

E'da notare infine che le considerazioni espresse nella presente comunicazione si riferiscono ai composti aventi reticoli ionici, non ai composti con legami omeopolari o a quelli con reticoli metallici.

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NEW SILICATE STRUCTURES

By N. V. BELOV

U.S.S.R.

ABSTRACT

In recent years the author has established several new silicate structures.

The structure of catapleiite, $Na_2Zr(Si_3O_9).2H_2O$ provides the second example of a metasilicate with threefold rings. The second example (after beryl) of a silicate with sixfold rings is dioptase, which has thus proved to be not an ortho–, but a metasilicate, $Cu_6(Si_6O_{18}).6H_2O$, with water of the zeolitic type in the large cavities between the rings.

In 1947–48 the ring structure of the Alpine beryllium silicate, milarite, $KCa_2(Be,Al)_3Si_{12}(O,OH)_{30}$ was demonstrated; the sixfold rings of this mineral were found to be twice as high as those of beryllium, with the formula $(Si_{6\times2}O_{18\times2}{}^{-6}) = (Si_{12}O_{30})$. Of the four oxygens around each Si, three are shared with the other silicons and not two as in metasilicates, which means that this is a silicate of the Si_2O_5 type, however, not of the layer but of the " Insel " type.

In the ramsayite (lorenzenite) $Na_2Ti_2Si_2O_9$, from Khibina, the existence of infinite metasilicate chains $(SiO_3)\infty$ of the pyroxene type has been proved, contrary to a ratio of $Si : O = 1 : 4\frac{1}{2}$ in the gross weight formula. Three oxygens of every nine are not linked to silicon but link only atoms of titanium and sodium. These latter also form chains, approaching magnesium chains in the same pyroxenes.

COSMOGONY AND GEOCHEMISTRY

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ABSTRACT

An attempt is made to describe geological evolution as a link in cosmic evolution. Stages of cosmic evolution are distinguished with emergent leading principles. In stellar evolution, the course of the process is determined by nuclear reactions; in the development of planets the reactions between the outer electronic shells play a dominant rôle (geochemistry).

Discussion of the origin of the planetary system, the formation of primordial planetary globes of gaseous solar matter, contraction and fractional condensation of the latter, the expulsion of the moon according to a combination of the tidal and resonance theory of G. H. Darwin and Jeffreys with the rocket principle.

The deductive reasoning gives a postulate about the initial state of the earth at the beginning of the geological history (anhydric phase). Further deduction leads to prognostic conclusions about the character and course of the endogenic process. These deductions can be tested and corrected by the diagnosis of the actual state by geology and geophysics. The source of endogenic forces is the energy liberated by irreversible, physico-chemical chain-reactions.

Thus we obtain a consistent explanation of the cause and interdependence of such phenomena as orogenesis, epeirogenesis, growth and decay of the sialic crust, gravity anomalies, deep-focus shocks, etc.

I. INTRODUCTION

GEOLOGICAL evolution forms a link in the evolution of our cosmic system. Therefore, a theory on the evolution of our planet has to fit into our general conception on the development of the universe. The initial stage of planetary evolution is the result of the preceding evolution of the sun and we can obtain some insight about this stage by means of the science of astrophysics. The final stage can be studied by the sciences of geophysics and geology. Between both there is a large gap in our observations. Two methods can bridge this gap between stellar and planetary evolution. We can start from the former process and extrapolate it by deductive reasoning, according to the general laws of physics and physico-chemistry. Or we can start from the present state of the earth and try to reconstruct older stages by means of inductively obtained geological laws. The best method is to work from both sides. The correctness of the deductive way of reasoning can be tested by geology, and that of the inductive way by the postulate obtained from heliology.

When we try to reconstruct the situation at the beginning of geological development by means of the inductive method alone, we can never be certain about the correctness of our conception because many ways of evolution, starting from quite different initial situations, may have led to the present one.

When following the inductive way of reasoning and extrapolation the question always arises whether the conceptions about the initial situations are in harmony with the preceding stellar and planetary evolution. The cosmogony of our planetary system provides the postulate for the ensuing geological evolution. From this initial stage the latter can only evolve along one main way, according to the general physical and physico-chemical laws, leading on to the present situation. The coercive course of the further evolution, when starting from a given postulate about the initial stage of a system, is a great advantage of the deductive way of reasoning. It provides a number of tentative prognostic conclusions, which can be tested by geophysical and geological observations. Therefore, it is desirable to obtain a conception about the initial stage of the earth as the result of the preceding cosmogony. This is attempted in the following pages.

II. COSMIC EVOLUTION

It is possible that Einstein's static model of the Universe (with finite concentration of matter), and de Sitter's model (with red-shift in the light of distant particles but no finite concentration of

matter) might really correspond to a considerable extent with the initial and final states of the actual universe. However, our present data are insufficient to provide a precise cosmological model which would necessarily correspond to the actual universe in all regions and over all time-intervals.

But the data about the part of it which can be phenomenologically studied allow some general statements, such as the main laws of thermo-dynamics. In each state of the cosmic evolution the free energy accomplishes a certain organization increasing the entropy and giving rise to a hierarchic system of stages of evolution. In this hierarchy the basic units develop into higher states of organization with emergent new principles of evolution. In other words, for the higher states all the natural laws of the lower one are valid, beside some new principles which are characteristic (emergent) for the higher state of organization.
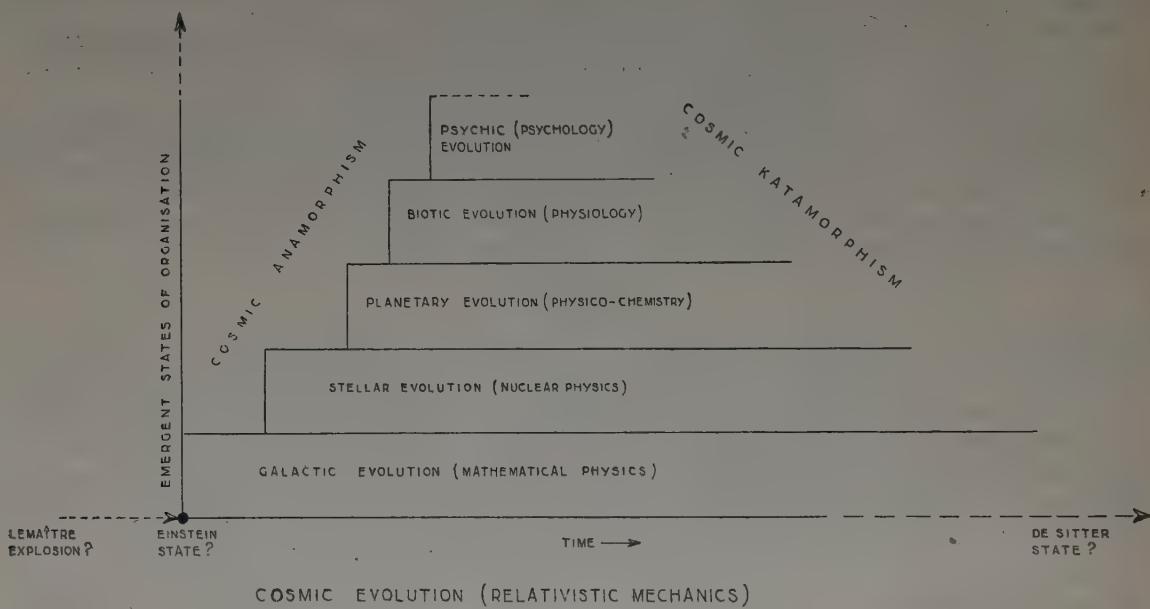
FIG. 1.—*Hierarchy of the states of cosmic evolution.*

For instance, nuclear reactions are the leading principle in stellar evolution (astrophysics), whereas reactions between the electronic shells of the elements determine the course of planetary evolution (physico-chemistry).

Under favourable conditions the physico-chemical flow of free energy may assume a canalized course, giving rise to living creatures with metabolism (selective assimilation and dissimilation).

Finally, the " symbolic knowledge " (Eddington) might be another emergent principle of evolution in the psychic state of development.

Natural Science strives for a uniform way of description of the universe by means of symbolic knowledge. For such a description the hierarchy of the states of organization has to be taken into account.

The emergent principles of biological evolution do not affect the planetary evolution; but the natural laws of the latter are also valid for life.

In the same way the principles of physico-chemistry, which play a leading rôle in planetary evolution are of no importance for stellar development; but the natural laws of astrophysics are also fundamental for geophysics.

The transitions of a state of evolution to the next higher one form the critical movements in the

whole process; transition of galactic nebulae into stars, formation of a planetary system from a star, origin of life on the earth, and creation of psychic entities.

Geologists are specially interested in the cosmogony of our planetary system in relation with the postulate for the initial state of the evolution of the earth. Many theories have been advanced, but as yet not a single one is entirely satisfactory. Perhaps a solution might be found with the aid of recent astronomical observations on planetary nebulae.

According to the Russell diagram the contraction of spherical gas masses (giants) changes potential energy into kinetic energy (heat) and radiation energy.

Due to the rise of temperatures and pressures in the internal part of the stars transmutation energy is liberated also by nuclear chain-reactions. The radiation pressure rises and, finally, it becomes as large as the force of gravitation so that no further contraction is possible. Then cooling begins and the stars evolve into dwarfs along the main branch of the Russel diagram.

At the stage of development when the radiation pressure counterbalances the force of gravitation, a meta-stable situation may originate. When the enormous production of transmutation energy cannot be liberated by radiation, first pulsations enlarge the radiating surface. But when this means is also insufficient Nova-explosions may occur. Gaseous matter is expelled with radial velocities of about 1,000 km. per second. Besides the relatively small gas shells expelled by Nova-explosions, larger gas rings are known called planetary nebulae. The latter have diameters of $0 \cdot 05 - 1 \cdot 00$ light-years, densities of 10^{-20} grams per cm³, and central stars of the O and W spectral types.

The expelled gas of Novae is of the order of 10^{-5} masses of the sun and that of radiating parts of planetary nebulae is 10^{-2} masses of the sun (their total mass is presumably some dozens of times larger). The radial velocities of planetary nebulae are of the order of 10 km. per second (4—50 km. per second).

The relations between Nova gas-shells and planetary nebulae are not yet well known. The Crab Nebula in Messier 1 (N G C 1952) is the result of a super-Nova-explosion in 1054 and is still expanding with a velocity of 1000 km. per second. This nebula must have a large mass otherwise its speed would have been checked by the interstellar gas. It is conceivable that super-Novae explosions produced planetary nebulae.

The size of our planetary system is between those of the Nova gas-shells and of the planetary nebulae. Therefore, it might be suggested that in some cases the masses of the expelled gas shells and their initial radial velocities were such that an equilibrium was reached; gas rings originated which rotated at fixed distances around the central star. Then a system would have been formed comparable with the cosmogenic conception of Kant and Laplace.

Afterwards these gas rings would concentrate around their densest parts, forming planets. Such a line of thought would explain our planetary system as a normal, monoparental product of stellar evolution.

A difficulty for such a concentration would be the absence of a centre of gravitation. R. Schwinner (1936, p. 45 et seq.) pointed out that a planetary gas-sphere, a miniature star of the Eddington-model, could not exist due to the small mass of the planets. It should have very low temperatures, but then the Fe, Ni, SiO_2 and other oxides would not be present in a gaseous state. Could it be that meteoric masses, belonging to our solar system, acted as centres of condensation in these planetary nebular rings? Such a solution has been suggested by Schwinner (1936, 1. c, p. 310, 313).

The biparental formation of our planetary system according to the collision theory of Moulton and Chamberlain is at present preferred by many authors. The chance is very small that such a collision or near passage between our sun and another star has occurred during the time available for the evolution of our galaxy, even if we take into account the reduced dimensions of the universe some thousands of million years ago (Principle of the expanding Universe). According to such a collision theory our planetary system would merely be a whim of Nature. However, the law of Titius and Bode is opposed to such a haphazard way of origin, as is suggested by the biparental or collision theory.

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This law indicates that our planetary system is the result of organization according to general physical laws; in other words, a more or less monoparental solution has to be preferred.

In relation with the problem of the initial state of the planets we can leave unanswered for the moment the question whether our planetary system had a biparental or a monoparental origin. Nearly all cosmogonic conceptions, thus far proposed, lead to the postulate that the planets were formed from spherical masses of solar gases, which concentrated and condensed around primary or foreign centres of gravitation.

III. PLANETARY EVOLUTION

The gaseous clouds of solar matter forming the primeval stage of the planets will at first have been cool. Thereafter, the concentration of the gaseous matter around denser masses started transforming them into gaseous globes, rotating around the parental star.* It can be supposed that the contraction of the cool and rarified spheres of solar matter will again cause a rise of temperature. On account of the much smaller dimensions of planetary gas spheres, as compared with stellar gas masses, the resulting pressures and temperatures will be thousands of times lower than in stars. Whilst in the latter nuclear reactions (forming complex elements) are the most typical process, in planetary gas spheres only reactions between the electronic shells around the nuclei of the elements occur (besides spontaneous radio-active disintegration of certain elements and their isotopes). In other words, the chief difference between the stellar and the planetary evolution is that the former is governed by nuclear physics and the latter by chemical reactions. Therefore, geochemistry is a fundamental science for our knowledge of the evolution of the earth.

IV. FRACTIONAL CONDENSATION OF THE PLANETARY GAS-SPHERE

The temperature of the contracting sphere of gaseous solar matter which formed the initial state of the earth may first have risen to about $10,000°$ C.; thereafter radiation will have caused a rapid cooling. It is clear that the lighter elements, especially hydrogen, were partly dissipated into space during the maximum temperatures, owing to the relatively small magnitude of the force of gravitation. This explains the difference between the mean composition of the outer part of the sun (according to Russell), and that of the earth (according to the calculations of Niggli, Washington, and Linck).

Kuhn and Rittmann (1941) reject Goldschmidt's hypothesis that a liquid earth-sphere has split up into an iron core, an oxysulphide shell and a silicate mantle. They suggest that the core of the earth still consists of solar matter in a highly compressed, supercritical state. This core is surrounded by a magmatic sphere of molten silicates and the outer shell is formed by a solid crust.

Provisionally we may leave unanswered the question whether the core of the earth has maintained the mean composition of the original gaseous solar matter or whether it is composed of a denser meteoric mass of Fe and Ni. But it is indeed highly improbable that the primeval gas-sphere first condensed into a liquid sphere and that thereafter a liquidation of this melt occurred as was suggested by Goldschmidt. In the case of the blast furnace process we start with solid material, which is rendered molten, and then liquidation occurs into pig iron, matte and slag. In the case of the formation of the earth quite the reverse path was followed.

For the earth, the initial state was that of a more or less homogeneous gas-sphere, the condensation of which produced a layered liquid sphere. This layered structure of the earth is most probably the result of a *fractional condensation* of the primeval gas-sphere during its cooling (by radiation and by evaporation of the lighter elements into space).

During this condensation the earth's shells successively came into existence. The condensation depends on the partial pressures of the elements and their compounds in the gas and on their boiling temperatures under the then existing general conditions of pressure and temperature.

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*MERCIER (*Nature*, vol. cxli, p. 201, 1938) estimates that the diameter of the primordial globe or polytropic gas sphere from which the earth has been formed had a radius of 124,000-220,000 km. (mass 6×10^{27} gm., central temperature about $6,000°$K, corresponding with the effective temperature of the sun at time of formation).

The probable succession of the formation of compounds and their fractional condensation has yet to be studied by means of physical and physico-chemical calculations. Besides temperature and pressure many factors have to be taken into account such as: (1) the percentage of an element in the primeval gas-sphere, (2) the radius and electro-chemical valency of the ion (Coulomb forces), (3) the number of atoms in the compound, (4) the enveloping of the central positive ions by negative ions, (5) the Van-der-Waals forces in the liquid phase (cohesion).

Tentatively the following provisional picture of this process of fractional condensation might be given.

At the maximum temperature of the gas-sphere chemical compounds could not yet exist. The gas consisted of mono-atomic and ionic particles. Those with the smallest radii and the highest partial pressures will have concentrated in the central part of the gas-sphere, (iron atoms and ions, and the other siderophile constituents). This central part was highly compressed forming the earth's core, consisting of mono-atomic and ionic matter in a hypercritical state. Its temperatures might be as high as 12,000° C. according to Kuhn and Rittmann (1941, p. 246).

With falling temperature bi-atomic compounds, especially those held together by two or more chemical valencies, could be formed in the gas. These attained such high partial pressures that their condensation ensued (compounds of chalcophile elements). Thus the intermediate shell of molten matter came into being.

At still lower temperatures also pleo-atomic compounds of lithophile elements became relatively stable, especially SiO_2. When SiO_2 molecules once condensed they were firmly kept in the belt by Coulomb-forces due to the formation of $[SiO_4]^{4-}$ ions. The condensed matter assumed subsilicatic composition (sifema). The gradual transition between the di-atomic, intermediate shell and the silicate mantle is presumably situated at a depth of about 1,200 km. beneath the present surface.

It can be supposed that during the first stages of the condensation of the silicate mantle the viscosity of the melt was still relatively low. Consequently, convection currents could stir the melt, giving it a homogeneous composition. The decreasing temperature and pressure of the remaining gaseous envelope caused a boiling up of the more volatile constituents. This caused perhaps two-phase convection currents by the foaming up of the melt, which was at the boundary of the equilibrium between gas-liquid. The more volatile constituents escaped again into the remaining part of the hot and heavy gas mantle. Thus the equilibrium between the melt and the gaseous envelope could be fairly well maintained for some time.

But with further decrease of temperature the silica content of the melt increases more and more and also Al_2O_3 was incorporated in it. The outer shell of condensation was saturated with silica. Chains and plates of complex ions were formed in the melt, and due to the increasing size of the molecules the Van-der-Waals forces became more and more important. This gave a rapid increase of the viscosity during the condensation of the last few hundreds of kilometres of the silicate mantle. This outer shell might be called " sialma " or " salsima." In this salsima stage of condensation the retrograde boiling, effective during the condensation of the sifema, came more or less to a halt. A free exchange of constituents between gas and melt was no longer possible. The cooling of the deeper parts had to occur chiefly by conduction, so that in this outer shell steep temperature gradients came into being.

V.   HYPO-VOLCANISM AND THE BIRTH OF THE MOON (SELENOLOGY)

The decreasing pressure and temperature of the gaseous envelope of the earth caused an over-saturation of the more volatile constituents in the silicate melt. But the viscosity of the salsima shell hampered their escape by retrograde boiling, in contrast to the situation during the condensation of the sifematic melt.

Meanwhile the earth was rotating in the gravity field of the sun*, so that the silicate mantle was

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*One rotation in about four or five hours, according to G. H. Darwin's calculations. The ratio between the tidal forces of the sun and the moon is at present 1 : 2·3.

FIG. 2.—*Birth of the moon.*
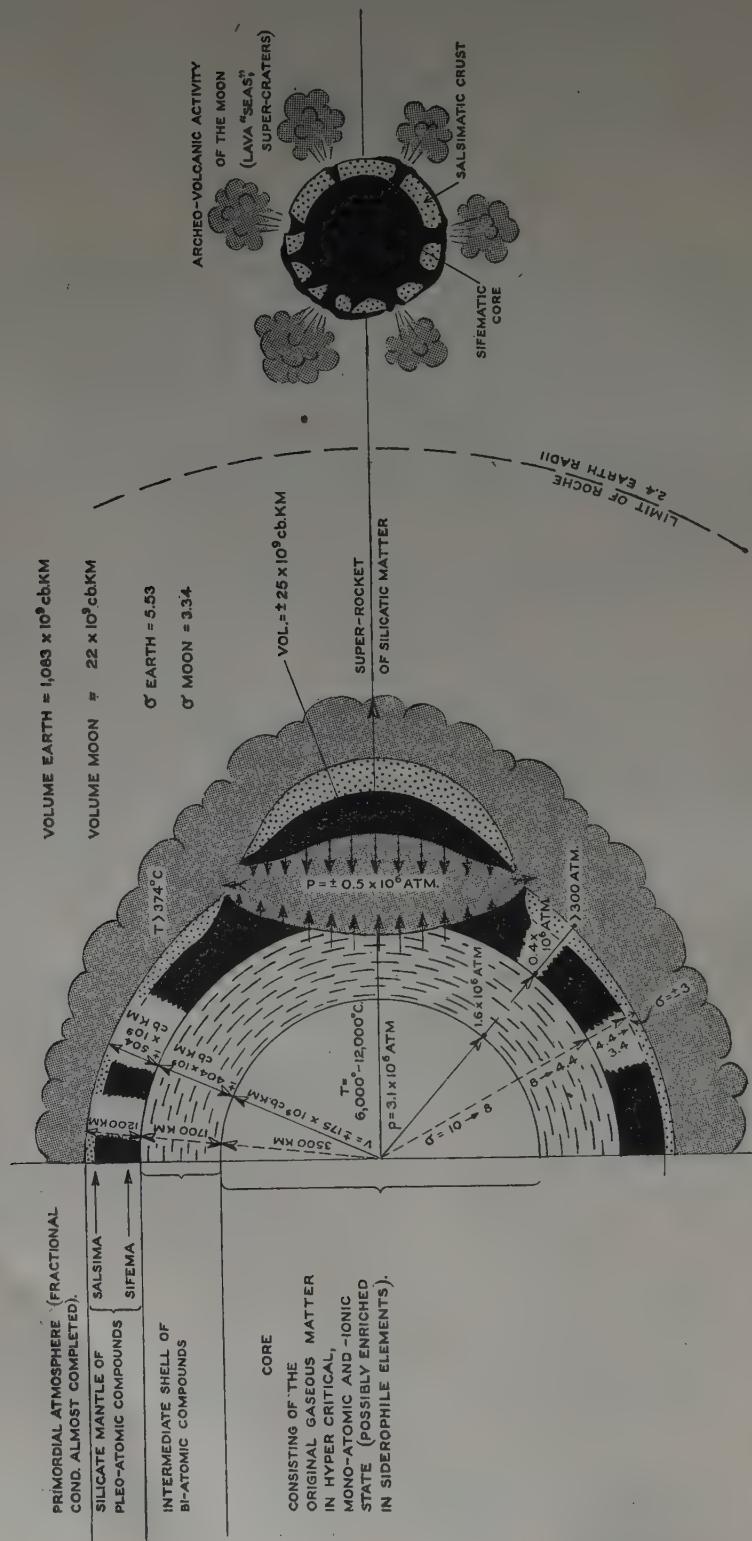
periodically subjected to decrease and increase of pressure by tidal waves. The accumulation of volatile constituents at its base (perhaps largely hydrogen from the inner part) caused finally a foaming up by the pull of the tidal waves. This foaming up more and more increased the height of the tidal waves in the silicate mantle. The blisters occasionally burst open and terrific volcanic explosions occurred, emitting gases of sifematic matter through temporary rifts in the viscous salsimatic shell, and throwing up large slabs of salsima.

The liberation of volatiles from the deeper levels, breaking through the highly viscous sphere of salsima, caused a phase of deep-seated violent hypo- or archaeo-volcanic activity. The acme of this archaeo-volcanism, aided by the pull of tidal waves at the equator, may have caused the expulsion of a part of the silicate mantle. An enormous blister forming the top part of the tidal wave was shot like a huge rocket outside the limit of Roche (2.4 times the radius of the geoid)* by means of the explosive volatization of the sifematic matter at its base.† Thereafter the silicate slab assumed (by its own force of gravitation) a spherical shape, thus becoming our satelite the moon, with a specific density of 3.34. This conception of the origin of the moon is a combination of the tidal and resonance hypothesis (by G. H. Darwin and Jeffreys) with the rocket principle.

Such a formation of satellites by a physico-chemical meta-stability in the final stages of the condensation of planets would be to a certain extent, although on a much smaller scale, a repetition of the formation of planets by stars due to nova-explosions and the expulsion of planetary nebulae, as suggested in Section II. The planetary masses were expelled from the sun in a gaseous state and the moon was detached from the earth in a liquid state.

The earth mass had still enough free energy to continue its evolution after the pyrospheric phase with hypo-volcanism. This energy caused the geological development with cycles of mountain building and the present epi-volcanism. The amount of free energy in the mass of the moon was too small for such a subsequent evolution. Its development stopped after the release of its volatiles and it quickly cooled down to a rigid sphere of silicate glass, deprived of its more volatile constituents. The volcanic scars on the surface of the moon are comparable with the picture of the face of the earth during its pyrospheric stage of evolution with hypo- or archaeo-volcanism.

The healing of the wound in the side of the earth occurred by plastic deformation of the sifema shell, but it caused deformations of a tougher nature in the highly viscous salsima shell. The latter covered only the marginal parts of the Pacific which is supposed to be the site of the moon-expulsion (Fisher, Pickering). The distortions and dilatations of the sialsima shell during the expulsion of our satellite at the end of the pyrospheric stage of development might have produced the fundamental geotectonic pattern of the earth.‡ This pattern predestined the course of the ensuing geological evolution and orogenesis.

VI.   COSMOGONIC POSTULATE OF THE GEOLOGICAL STATE OF EVOLUTION

The foregoing deductive reasoning has led us to the following postulate about the state of the earth at the beginning of the geological evolution about 2×10^9 years ago.

At this stage the earth consisted of a core of solar or meteoric matter in mono-atomic and ionic state. This might be rich in hydrogen, perhaps some 30 per cent, as was suggested by Kuhn and Rittmann (l.c., 1941) and Kronig, de Boer and Korringa (1946) are of the opinion that this is physically possible when the hydrogen in the core is present in an atomic phase, passing at a depth of about 2,900 km. into a molecular phase. This core was surrounded by an intermediary shell of bi-atomic compounds (from about 2,900 km. to 1,200 km. depth), which passed outward into a silicate melt of

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*According to the *Encycl. math. Wissensch.*, the limit of Roche is 2·87 earth radii.

†SCHWINNER (1936, p. 310 *et seq.*) also suggests an explosive origin of the moon, by means of the expulsion of hydrogen from the inner part of the earth.

‡See figures 4 and 5 in the author's paper: " De physisch-chemische ontwikkeling der Aarde." *Geol. en Mijnbouw*, Jan. 1949.

CONTRACTION OF THE
PRIMORDIAL PLANETARY GAS-SPHERE
AND HEATING TO MAX. ±10,000°C.
TILL COOLING BY RADIATION AND
EVAPORATION OF LIGHTER ELEMENTS
PREVAILS.

INCREASING RADIUS
OF THE ELLIPTICAL ORBIT
BY TIDAL FRICTION. AT
PRESENT ± 60·3 EARTH RADII

CONSOLIDATED
MOON

SPHERICAL TRANSFORMATION AND
ARCHAEO-VULCANISM OF THE MOON

BEGINNING OF THE
FRACTIONAL CONDENSATION

LIMIT OF ROCHE
(2·4 EARTH RADII)

EXPULSION OF THE
MOON-ROCKET

PRIMORDIAL
ATMOSPHERE

SALSIMATIC SHELL (BASIC SILICATE MELT)

PLEO-ATOMIC COMPOUNDS OF
LITHOPHILE ELEMENTS

SIFEMATIC SHELL (ULTRA BASIC SILICATE MELT)

INTERMEDIATE SHELL OF BI-ATOMIC COMPOUNDS

MONO-ATOMIC CORE OF GASEOUS MATTER IN HYPERCRITICAL STATE, PRESUMABLY ENRICHED IN ATOMS AND IONS OF SIDEROPHILE ELEMENTS

±10,000°C.

±5,000°C.

±1,000°C.

±400°C.

42,000
KM

36,000

30,000

24,000

18,000

12,000

6,000
KM

0

- 2,500 MILL. YEARS ?

-2,000 MILLION YEARS ?

-1,000 MILLION YEARS

NEBULAR
STAGE

PYROSPHERIC STAGE
WITH ARCHEO-OR
HYPO-VOLCANISM

ANHYDRIC STAGE

GEOLOGICAL STAGE (S. STR.) WITH HYPO-DIFFERENTIATION AND EPI-VOLCANISM

HYDRIC STAGE

BIOTIC STAGE

Fig. 3.—*Development of the earth from a primordial gas sphere.*

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pleo-atomic molecules. The silicate mantle can be divided into a bathysphere of subsilicatic composition (sifema) and an outer shell of ortho- to meta-silicatic composition (sialma or salsima).

The latter was not evenly distributed on account of the expulsion of the moon. It varied in thickness presumably from one to two or more hundreds of kilometres. If present in the inner parts of the Pacific, it occurred there in a degenerated state, deprived of more volatile constituents. During the subsequent geological evolution the salsima of the Pacific area was not subjected to an important hypo-differentiation, but simply passed into the crystalline state down to a considerable depth. The primeval atmosphere at the initial geological stage still had a temperature of some hundreds of degrees (Rittmann, 1939).
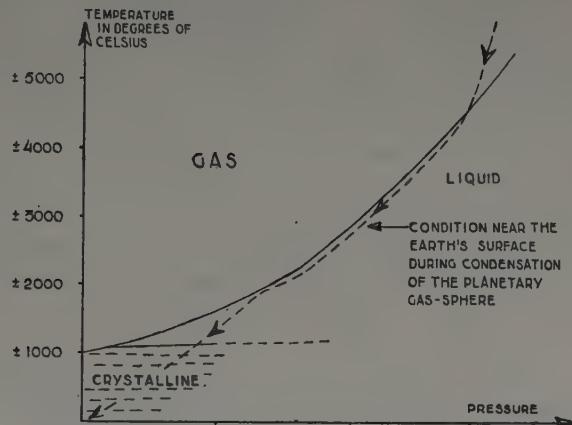

FIG. 4.—*Hypothetical graph of the conditions near the surface of the earth during the fractional condensation of the primeval gas sphere.*

VII.   HYPO-DIFFERENTIATION

The expulsion of the moon formed at the end of the deep-seated archaeo-volcanism, since then it was no longer possible for the volatile constituents in the sifematic part of the silicate mantle to break explosively through the salsimatic shell. The adjustments of the chemical composition of the melt to the changing conditions of temperature and pressure occurred thereafter chiefly by means of ionic and atomic diffusion. It is to be expected that the surplus of hydrogen, entrapped in the melt during the earlier stages of condensation of the planetary gas sphere, has a tendency to migrate upward and outward. Such a front of hydrogen emanations will have a positive charge and this electro-chemical field will influence other ions in the melt. Especially the small Si^{4+} ions (0·39 Ångstrom units) will be driven outward in front of it, moving through the spaces between the large oxygen ions (1·35 Å.u.)*. Such ionic diffusions will cause a differentiation of the salsima shell. The lower section of the latter, deprived of part of its silica-content, will become ultra-basic (simatic) and the higher section intermediary to acid (sialic). Such a disperse diffusion-differentiation provides a tendency to form a layering in the outer salsimatic shell.

Such deep-seated processes of chemical differentiation, either by diffusion or by gravitative crystallization differentiation, might be called " hypo-differentiation," distinguishing them from the shallower processes of " epi-differentiation " of intra-crustal magmas, which are studied as samples of igneous rocks.

VIII.   HYPO-DIFFERENTIATION AS THE SOURCE OF ENDOGENIC FORCES

Since 1931 the author has advocated the idea that the " hypo-differentiation " is the main source of the endogenic forces. The hypo-differentiation of the largely undercooled salsima shell will start

*Oxygen occupies 91·77 per cent of the space in the outer part of the silicate mantle (" oxysphere " of Goldschmidt).

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there, where the physico-chemical gradients of temperature and concentration are steepest. This will be in its thinnest parts, formed by the dilatations and distortions of this shell during the expulsion of the moon and the healing of the wound. From the axial zones of the primeval geosynclinal belts the exothermal process of hypo-differentiation will spread laterally, transforming the original salsima shell into the present layered composition of the tectonosphere. (Principle of the growth of the sialic crust during geological evolution.) This physico-chemical process will be accompanied by undatory deformations at the surface (orogenesis).
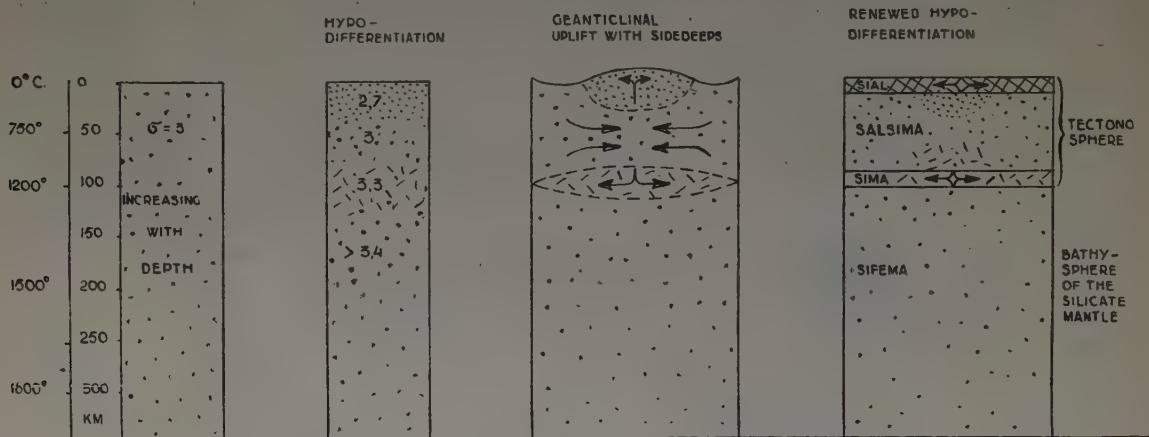

Fig. 5.—*An orgenic cycle caused by hypo-differentiation. (Sial and sima-shells formed by previous cycles not distinguished.)*

Under the side-deeps of the uplift the salsima is subjected to a relief of pressure, and a steepening of the gradients of temperature and concentration. Consequently, there also the process of hypo-differentiation will be started. After an incubation period of some dozens of million years also under the side-deeps sialic roots (asthenoliths) and simatic antiroots are generated. Thus the impulse of orogenesis spreads laterally in ever widening arcs from foci of diastrophism (orogenic systems or undation systems).

Such wave-like deformations of the earth's surface by differential radial movements disturb, in their turn, the gravitational equilibrium in the crust and its sedimental epidermis. In other words, they form accumulations of potential energy. Gravitational reactions will set in, causing dilations of the uplifted belts and compression of the depressed ones. Such gravitational reactions cause tectogenetic deformations in the epidermal, dermal and bathydermal levels of the tectonosphere.

Thus we arrive deductively at the conception that depressed areas (geosynclines) are the birthplace of mountain systems, which is confirmed by the inductive diagnosis of geology. The roots of orogenic uplifts are formed by accumulation of sialic material from below. Such mountain roots, called " asthenoliths " by the author, might be compared with the natural roots of teeth, because they accumulate before the pressing up of a mountain range, just as the teeth are formed in the jaw before they grow out. This conception stands in contrast to the formation of mountain roots by crustal buckling, as conceived by Vening Meinesz. The mountain roots according to the buckling hypothesis are squeezed down into the substratum like the artificial roots of dowel crowns.

The bicausal interpretation of orogenesis and tectogenesis by endogenic differential uplifts on the one hand and gravitational reactions on the other, provides an unstrained scheme for the interpretation of the evolution of mountain systems. The interdependence of the processes of orogenesis, tectogenesis, volcanism, earthquakes, and isostatic anomalies can be consistently explained in this way. An example of such a bicausal interpretation of regional geological evolution is given by the author in his book on the Geology of Indonesia (1949).

IX.   HYPO-DIFFERENTIATION AS THE CAUSE OF EPEIROGENESIS AND DEEP-FOCUS EARTHQUAKES

The liberation of the physico-chemical energy of the salsima shell causes orogenesis, with rhythmic intervals of the orogenic phases of some dozens of million years. When this energy is consumed the period of mountain building, such as the Hercynian and the Alpine periods, comes to a temporary standstill.

However, the hypo-differentiation of the salsima shell is only a first stage in the tapping of the endogenic energies. When such a cycle is completed, cooling penetrates into deeper levels of the silicate mantle. The partly crystalline simatic shell of the tectonosphere, that is the layer between the seismic Mohorovičic discontinuity and the base of the tectonosphere at about 100 km. depth, will be heated from below and ultimately be remelted. Moreover, the upward diffusion of constituents from deeper levels continues, causing an enrichment of the sima with silicon ions and other constituents. The rise of temperature and the process of diffusion transform the sima layer into a kind of "sima-asthenolith," which is composed of regenerated salsima. This transformation of sima into salsimatic magma bears some resemblance to the transformation of the sialic crust into palingenic magmas by migmatitization. We might speak of "hypo-migmatitization" of the sima, distinguishing it from "epi-migmatitization" of the sial crusts by underlying asthenolithic roots of sialic magma.

At the surface the hypo-migmatitization will cause broad-warped tumescences of the epeirogenic type. The sialic crust will be corroded from below by activated and regenerated salsima. Finally, the salsima, contaminated by crustal matter, may reach the surface, giving rise to voluminous extrusions of plateau-basalts.

The effect of these magmatic processes is two-fold. In the first place, they cause a concentrated transport of energy to the surface, so that cooling prevails again. In the second place, the consolidated intrusions and extrusions of basalts cause an important increase of the mean specific density of the sialic crust, which disturbs the gravitational equilibrium. Therefore, in the final stage of such a tumescence of continental dimensions a break-down occurs, and the crust will sink down again, even to oceanic depths. Atlantis, Lemuris, Eris, passed through such major cycles respectively in Jurassic, Cretaceous and Lower Tertiary times (geo-undations, with a period of some hundreds of million years; decay of old continents).

Such extensive epeirogenic movements are accompanied by mass-displacements in the silicate mantle down to considerable depths below the tectonosphere (to which are restricted the mass-displacements accompanying the common orogenic processes). Zones of shearing-stresses originate, which dip from the margins of the subsiding continental blocks under the adjoining continents. In these zones the shearing stresses may locally accumulate so rapidly, that they cannot be released by plastic deformation. Intermediate and deep-focus shocks are the result. Such shocks will be found only in such areas, where geo-undatory movements are still in progress. Therefore, they are not found around the Atlantic basin, but they are a common feature around the Pacific, where border-continents are subsiding in the present state of the geological evolution.

X.   CONCLUSION

The salsima acts during geological evolution as a "cambium," being the formative layer of parental magma between the upper and lower layer of the tectonosphere (respectively sial and sima). The intermediate salsima layer is, to a certain extent, an intermediary station for the flow of energy from the inner parts of the earth to the surface, where the energy is finally radiated into space. The flow of energy from the inner parts of the earth to the surface is not a simple thermal phenomenon, as was thought by the adherents of the contraction theory. Neither is it a purely thermo-dynamic process, as is conceived by the supporters of the hypothesis of convection currents in the substratum. This convection hypothesis only takes into account the reversible expansions and contractions by variations of temperature and pressure. The evolution of the earth is essentially a physico-chemical process, a complex of exothermal chain-reactions due to (and retarding) the cosmic process of cooling of our planet. During geological evolution the flow of free energy is continually changing from one
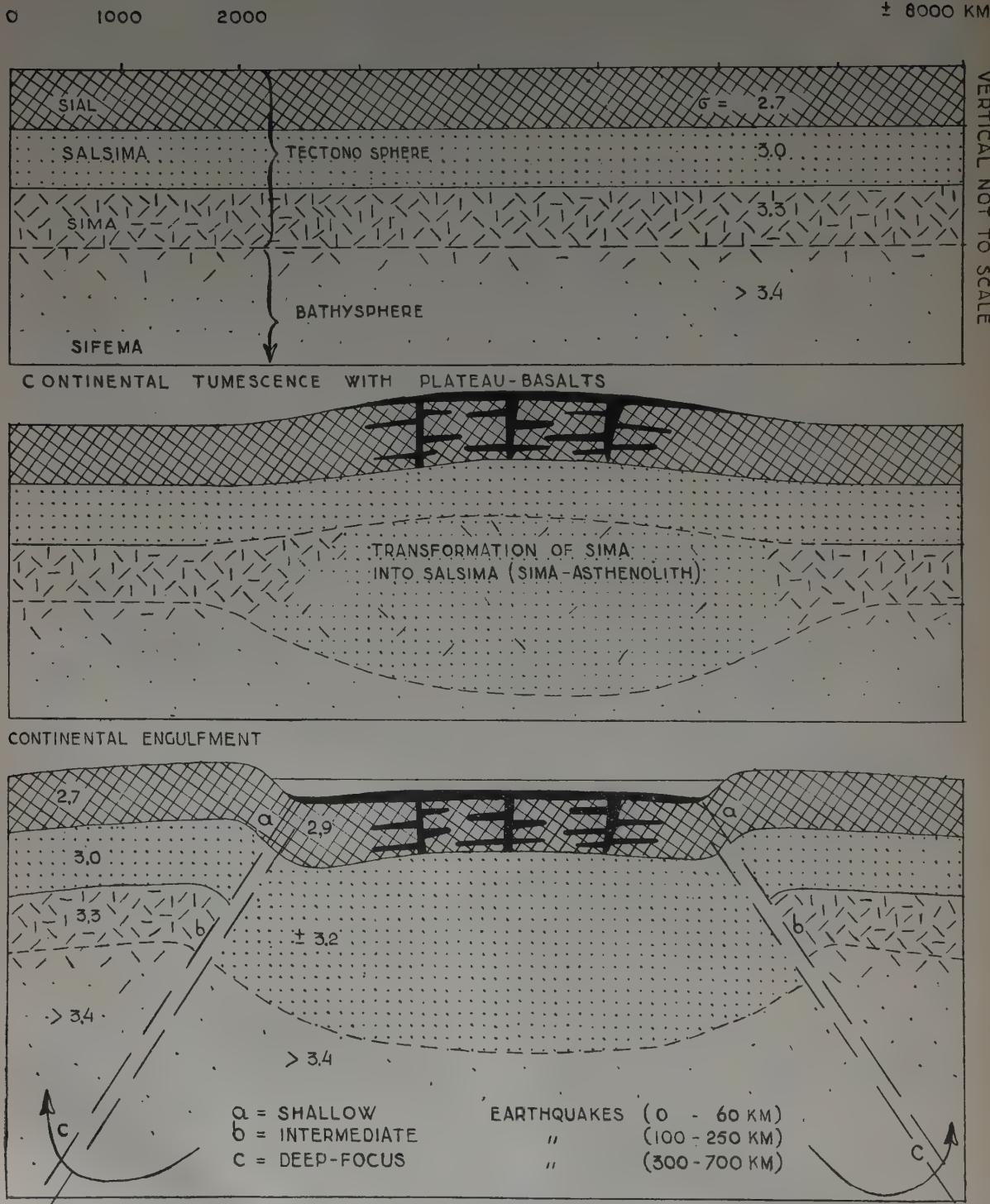
FIG. 6.—*A cycle of geo-undation by salsima regeneration.*

state into another. As on a Jacob's ladder, the constituents may ascend and descend by diffusion according to the existing physico-chemical gradients.

These physico-chemical chain reactions as a whole are irreversible because they occur according to the second main law of thermo-dynamics. The distribution and organization of primeval solar matter in the shells of the earth cause a general rise of the entropy of our planet, whilst the reserves of physico-chemical potential energy are gradually diminishing (ageing of the earth).

The main difference between stellar and planetary evolution is the much lower energy level of the latter. In stellar evolution the main source of energy is the transmutation energy liberated by nuclear reactions, whereas for planetary evolution reactions between the electronic shells of the constituents can be considered as the source of the endogenic forces.

Radio-active energy, liberated by nuclear disintegrations, may have been very important during the first stages of planetary evolution; for these unstable constituents are an inheritance of the preceding evolution of the mother star. But most of this heritage was spent in the earlier phases of planetary evolution. During geological evolution (*sensu stricto*) the liberation of physico-chemical energy by exothermal chain-reactions is the emergent leading principle.

Thus deductive reasoning from a cosmogonic point of view has led us to the conclusion that geo-chemistry is the fundamental principle for our understanding of geological evolution and the accompanying endogenic processes. The prognostic picture, tentatively arrived at, can be tested by geologic, petrologic, gravimetric, seismologic, and other observations. With the aid of these observations it is possible to trace the errors in the deductive extrapolations, thus accomplishing the necessary adjustments in our general conception of the evolution of the earth. The problem of origin and evolution of the earth is so complex, that for its solution we need the co-operation of specialists in various realms of natural sciences. This paper endeavours to stimulate such a co-operation by outlining a general working hypothesis, which still has to be tested in its many-sided aspects.

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DISCUSSION

J. P. MARBLE congratulated Dr. van Bemmelen on his masterly presentation of a very interesting theory. He had never listened to a theory of earth evolution and development that took into account so many petrologic and geologic considerations. A great deal of work should arise as the result of this paper, both by those who did not agree with the author's views, and by those who did. The results of Dr. van Bemmelen's views should be far-reaching.

ON GEOCHEMICAL TYPES OF OROGENIC ZONES

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ABSTRACT

Two principal geochemical types of orogenic zones may be distinguished. S. S. Smirnov, Member of the Academy of Sciences of the U.S.S.R., has designated them as the internal and the external zones of metallogenic belts. Within the external zones, the West-European and the East-Asiatic subtypes are distinguished.

The internal zones are characterized by an extensive manifestation of basic and ultrabasic magmas and of their acid sodium differentiates. Potash granites occur rarely, but alkaline rocks are rich in potassium.

In the external zones, basic and ultrabasic rocks are feebly developed. Potash granites are common. Alkaline rocks are represented by the sodium series.

The endogenetic mineralization of the internal zones is characterized by the metals of the Fe group, and of the group of Pt, Cu, Mo, Hg. Occurrences of Sn, W and Bi are insignificant. Characteristic of the external zones are Sn, W, Bi, Pb, Zn; Pt, Cr, and Ti are almost entirely absent.

The different geochemical types of orogenic zones differ in the nature of mineralizers as well. Characteristic of the internal zones are S, P, Ti; of the West-European subtype of external zones, O, F, CO_2; and of the East-Asiatic subtype, B.

The behaviour of iron is noteworthy. In the internal zones it forms accumulations of pyrites, titaniferous magnetite and apatite-magnetite ores; in the West-European subtype of the external zones, hematite and siderite ores; and in the East-Asiatic subtype, large accumulations of ferruginous tourmalines and chlorites, occasionally of pyrrhotite.

THE geochemical character of the geosynclinal zones and that of the orogenic zones derived from them, is dependent on the following three major groups of geological processes:—

- (*a*) sedimentation,
- (*b*) magmatic activity,
- (*c*) magmatogene mineralization.

The processes of sedimentation give rise to the main bulk of rocks; however, here such sharply pronounced geochemical differences which may serve as a base for the distinction of various geochemical types of the orogenic zones, are not observed. The magmatic activity proper leads to the formation of somewhat smaller bulk of rock masses, but in this case the geochemical differences between separate orogenic zones are more definitely pronounced. Finally, the processes of magmatogene mineralization give rise to comparatively small masses of rocks, but the latter show most distinctly expressed geochemical differences. As mineral deposits forming in this way are subject to commercial exploitation, the geochemical differences displayed by them in various types of orogenic zones present a world-wide interest. Insofar as these differences are not brought about independently, but are a result of geochemical differences observed in various magmatic rocks, the author finds it reasonable to begin this discussion by an examination of the magmatic activity.

For the geosynclinal zones and the orogenic zones arising from them, in their preliminary or geosynclinal period of evolution, effusions of basic lavas of spilitic form are characteristic. These lavas are frequently accompanied or alternate with intrusions of basic or ultra-basic magmas. The latter form ophiolitic belts of considerable length, being so characteristic of orogenic zones. On the other hand, the period of the final transformation of the geosyncline into an orogenic zone, is characterized by a marked development of large batholiths, built up of acid, for the main part potassium granitoids. These two types of magmatic phenomena, being rather different from the geochemical standpoint, are considered in general to be characteristic of all the geosynclinal-orogenic zones.

Upon close examination it becomes evident that in the prevailing part of orogenic zones both these types of magmatic phenomena are actually present, their distribution, however, being quantitatively very unequal. In those orogenic zones which are characterized by vast effusions and intrusions of basic magma of spilitic nature and by intrusions of basic and ultra-basic magmas, potassium granitoids are usually poorly developed. Conversely, in places, where the latter are widely distributed, the basic and ultra-basic magmas dating from the geosynclinal period of evolution are very scarce. The quantitative differences are often so sharp that they may serve as a base for considering these two groups of geosynclinal-orogenic zones as their two different geochemical types. This difference was originally pointed out by the late Russian academician S. Smirnov for the Meso-Cainozoic folded belt, skirting the Pacific. In this belt, being at the same time a metallogenetic belt, academician Smirnov distinguished two zones: (1) an exterior, the nearest to the continent, formed during the Mesozoic era, and characterized by a wide distribution of potassium granitoids with their peculiar metallogeny and by an extremely poor development of basic and ultra-basic magmas; (2) an interior zone, the nearest to the ocean, belonging to a younger age and formed in the time comprising the end of the Mesozoic and the entire Cainozoic eras; this zone is characterized by a wide distribution of medium, basic and ultra-basic magmas and by a markedly poor development of potassium granitoids.

An examination of other folded and metallogenetic belts shows that with a certain approximation such a subdivision can also be applied to them. To the type of interior zones of metallogenetic belts may be referred, for instance, the Scandinavian metallogenetic belt (Caledonides of Norway), the Meso-Cainozoic zone of the Mediterranean belt (the south of Europe, the Balkan Peninsula, Turkey, Transcaucasus, Iran), the eastern slope of the Urals, the metallogenetic belt of the Sayan Mountains (Siberia) and some others. To the geochemical type of the exterior zones belong, besides the Mesozoic folded zone of the Pacific belt, the Variscan folded structures of Central and Western Europe, the western slope of the Urals, etc. It is to be noted that according to the author's conception the interior and exterior zones are not parts of a single geosyncline, but represent independent geosynclinal zones, which are successively formed in different periods of time within the limits of larger structural units, defined by the author as geosynclinal and metallogenetic belts. Not entering into discussion of the inter-relations between the exterior and interior zones in time and space, the author will apply later on these terms only to definite geochemical types of orogenic zones. Let us try to give their comparative geochemical characteristics, primarily from the standpoint of magmatic activity, and then from that of metallogeny.

Extremely characteristic of the interior zones of metallogenetic belts in their preliminary stage of geosynclinal evolution are vast effusions of basic magmas. These magmas are usually represented by spilites, porphyrites (andesites), and rather often also by more acid rocks, belonging to the albito-phyre and quartz albitophyre types. This is a well known spilitic magmatic formation. Such are the Pre-Cambrian and Lower Palaeozoic lava flows of Norway, the Silurian and Devonian lavas encountered on the eastern slope of the Urals, the Cambrian lavas of the Sayan belt, the Meso-Cainozoic lava flows of Southern and South Eastern Europe and South-Western Asia (Turkey, Caucasus, Iran) and also the lava flows of the Pacific coastal zone of Asia and America.

A characteristic feature of all orogenic zones with abundant effusions of lavas of the spilitic formation is the wide distribution of basic and ultra-basic magmas and of their differentiates, occurring also in the form of intrusions. These intrusions usually alternate with superficial flows and are often connected with phases of folding which sometimes interrupt, but do not entirely stop, the process of the geosyncline evolution. Here belong primarily ultra-basic intrusions, often giving rise to ophiolitic belts of considerable length. Such is for instance the Mediterranean ophiolitic belt, spreading with some interruptions from Southern Europe to the islands of the Malay Archipelago, the ophiolitic belt of the Urals, the Sayan belt and many others. In the same orogenic zones, besides ultra-basic intrusions, there are usually encountered intrusive complexes which are mainly represented by basic rocks and rocks of medium acidity, with a subordinate development of acid rocks. Characteristic of

the latter is, in the majority of cases, a marked predominance of sodium over potassium. Owing to this, rocks of the trondhjemite or plagiogranite type play among them an important rôle. To such intrusive complexes belong in the first place the well known anorthosite-charnockite and the opdalite-trondhjemite groups of Norway, the numerous gabbro-diorite and plagiogranite intrusions of the Urals, the Kuznetsk Alatau, the Sayan Mountains, the Balkans, Asia Minor, the Caucasus and the Pacific coast of America, etc. In all these cases a close genetic connection of the acid (essentially sodium) rocks with more basic rocks is observed.

The common granitoids, rich in potassium, not connected genetically with the basic rocks, are most characteristic of such stages of the tectono-magmatic cycle as are associated with the final transformation of the geosyncline into an orogenic zone. In the orogenic zones of the type under examination these granitoids are usually scarcer in comparison with orogenic zones of other types. Their localization is much narrower in time and space than that of the basic intrusions and of their differentiates. Whereas the latter are distributed throughout the whole area of the orogenic zones belonging to the type discussed, and occur repeatedly during long intervals of geological time, the intrusions of potassium granitoids, on the other hand, correspond to one or two of the last phases of folding and are mainly confined to separate, most deep downwarpings, retaining their ability longer than the other parts of the orogenic zones.

As a characteristic example of the above may be cited the folded zone of the Urals. Here intrusions of basic and ultra-basic magmas accompanied by their more acid, essentially sodium, differentiates, took place repeatedly during the Silurian, Devonian and Lower Carboniferous periods, on the whole area of the folded zones of the eastern slope of the Urals. Intrusions of potassium granitoids, genetically not connected with basic magmas, occurred only in the Upper Carboniferous, and only in a definite deepset downwarping along the eastern slope of the Urals.

Very characteristic for this type of orogenic zones is the development, besides the basic and acid, also of alkaline magmas. The latter are usually grouped into two series: the potassium and the sodium series. It must be noted that the differences between them are most distinct in the more basic rocks, namely in the alkaline gabbroids and basaltoids. In the more leucocratic rocks, these differences are much less pronounced, and the alkaline rocks with a composition close to an eutectic one (phonolites, nepheline syenites), are often identical in both series.

In orogenic zones of the type of interior zones we see the development of sodium as well as of potassium alkaline magmas. The latter, however, are more characteristic. In effusive facies they are represented by leucitic rocks, potassium trachytes, phonolites and other rocks rich in potassium; in intrusive facies by shonkinites, monzonites, pseudo-leucitic rocks, potassium foyaites and others. Leucitic lavas and other effusive rocks rich in potassium which are associated with them are extremely characteristic of the last stages of volcanic activity of the Mediterranean orogeny. Here belong the leucitic lavas of Italy, Yugoslavia, Turkey, Caucasus, Iran and of the islands of the Malay Archipelago (Java, Borneo, Celebes and others). These alkaline rocks, rich in potassium, are traced here so regularly, that they ought to be regarded as not less characteristic of the Mediterranean orogenic zone, than its ophiolitic belt.

In the interior zone of the Pacific belt, not only the potassium but in general the alkaline magmas, are considerably scarcer. This can most probably be explained by the fact that the magmatic activity of the interior zone of the Pacific belt, in most of its regions, did not reach in its evolution the stage of the development of alkaline magmas. The correctness of this assumption is confirmed by the intense recent volcanic activity of this zone, with effusions mainly of basic and medium magmas ordinarily preceding the effusions of alkaline magmas, as one can judge from the example of the Mediterranean and other belts. It ought to be noted that in some of the isolated downwarpings, lying somewhat aside of the interior zone of the Pacific belt and which have undergone a more rapid evolution in their magmatic activity, the effusions of basic and medium magmas are already substituted by effusions of leucitic lavas (for instance the eastern outskirts of the Great Chingan in Manchuria,

the basin of the Great Anui River). Isolated occurrences of leucitic lavas are also found in some other parts of the interior zone of the Pacific belt (in New Zealand, California, Antarctica, etc.).

Within the Scandinavian, Uralian and the Sayan belts the alkaline rocks are mainly represented by nepheline syenites, but it is possible that the leucitic rocks of Scotland and of the Northern Kazakhstan (Ishim) are connected with the evolution of the magmatic activity of these belts. Concerning the Urals, we may also note here an intense development of potassium lavas of rather high alkalinity (trachytes) in the Upper Ludlow stage.

The other type of orogenic zones, defined above as the exterior zones of the metallogenetic belts, show quite a different character of magmatic activity. In the preliminary period of the evolution of geosynclines, there are also effusions of basic and medium lavas sometimes together with their acid differentiates. However, in a quantitative sense, the difference between them and the first type of orogenic zones is notorious. Here the basic effusions of the preliminary period are confined to narrowly limited periods of time, are much more narrowly located in their area of distribution, and play a markedly subordinate rôle in the general thickness of the stratigraphical succession. Such are the Variscan folded zone of Central and Western Europe, the Variscan folded zone of Mongolia, the western slope of the Urals, the Mesozoic folded zone of Eastern Asia, etc. In the immensely vast regions of the latter the effusives of the preliminary period are practically absent and the superficial volcanic activity begins here, in the main, only after the transformation of the geosyncline into an orogenic zone.

In full accordance with this fact is the poor development of the basic and ultra-basic intrusions in the exterior zones of the metallogenic belts. They never form here widespread belts and are encountered only in separate regions of limited area. They are almost entirely absent in the Mesozoic folded zone of Eastern Asia, not taking into account the small hypabyssal intrusions formed in the very late stages of the evolution of the orogenic zone.

Conversely, the intrusions of potassium granitoids are extremely characteristic of the orogenic zones of this type. Here they are distributed over a vast area and occur in connection with the numerous successive phases of folding. Such are the numerous Variscan granitoid intrusions of Central and Western Europe, the Variscan granitoids of Mongolia, and especially the Mesozoic granitoid intrusions of Eastern Asia.

Alkaline rocks rich in potassium are less characteristic of the orogenic zones of this type than of the zones of the first type. Sometimes there occur nepheline syenites. But the most typical of all the alkaline rocks are probably the melanocratic alkaline rocks of the sodium series, belonging to the type of essexites, teschenites, crinanites, etc. They form in the late stages of magmatic activity in these orogenic zones, mainly in their forelands, although often enough, they are also met with within these zones themselves. Such are the Carboniferous teschenites and other related rocks of Scotland, the teschenite intrusions of the western slope of the Urals and of Mongolia and the extremely widely distributed Upper Mesozoic (to Cainozoic) teschenites of North-Eastern Asia.

Thus, although in the two types of orogenic zones distinguished by the author are represented qualitatively more or less the same groups of magmatic rocks, both effusive and intrusive, their quantitative development is totally different.

In the effusive and intrusive activity of the first type of orogenic zones (the interior zones of the metallogenetic belts), there is a distinct prevalence of basic and ultra-basic magmas, magmas of medium acidity and partly of alkaline potassium magmas. In the second type (the exterior zones of the metallogenetic belts) potassium granitoids predominate and in part also alkaline sodium rocks. In the first type the most intense stage of magmatic activity corresponds, on the whole, to the geosynclinal period of evolution, including here the phases of folding which sometimes interrupt this period. In the second type this intense stage of magmatic activity corresponds to the period of transformation of the geosyncline into an orogenic zone and of subsequent evolution of the latter.

If the quantitative differences in the character of the magmatic activity, observed in the two types

of the above mentioned orogenic zones, are sufficiently distinct, the differences in their magmatogene mineralization can be traced still more definitely.

Especially characteristic of the interior zones of the metallogenetic belts are magmatogene deposits genetically connected with the basic and ultra-basic magmas and magmas of medium acidity and, in part, with their more acid, essentially sodium differentiates. The most characteristic metals are: platinum, chromium, titanium, nickel, iron, copper, partly molybdenum, cobalt, zinc, lead, mercury and arsenic. On the contrary, metals characteristic of the acid potassium magmas—tin and bismuth, are not very typical. Of the greatest economic value are magmatic, hystero-magmatic and contact-metasomatic deposits, disseminated ores, sulphide lodes, and only in part, vein deposits.

To deposits occurring in the orogenic zones of this type belong the chromium deposits, and here belong also the rich magnetite deposits. Very characteristic of this type of mineralization are the copper-nickel sulphide ores. Still more characteristic and widely distributed are the copper-pyrite and the iron pyrite deposits, representing the most typical metallogenetic feature of all the orogenic zones belonging to this type. The lead and zinc deposits in the orogenic zones of this type are also mainly represented by sulphide lodes and by a markedly subordinate number of vein deposits. As well as copper, which is one of the most characteristic metals found in orogenic zones of this type, other types of deposits play an important rôle, namely, disseminated ores, stock-works and vein deposits.

The distribution of precious metals (gold, silver) in different types of deposits is subject to considerable variations in different metallogenetic provinces of this type. On the contrary, for the young metallogenetic zones of this type (the Meso-Cainozoic zone of the Mediterranean belt and especially the Cainozoic zone of the Pacific belt), high concentrations of gold and silver in epithermal deposits are extremely characteristic (Transylvania, Turkey, New Zealand, Japan, North America and South America). Also it must be mentioned that to the same metallogenetic zones are confined typical subvolcanic deposits of mercury and arsenic (Italy, Yugoslavia, the Western States of the U.S.A., etc.).

Of great interest is the behaviour in the metallogenetic provinces of this type of those metals, which are regarded as typical for the acid potassium magmas, i.e., of molybdenum, tungsten, bismuth and tin. Among them, molybdenum is the most typical for provinces belonging to the interior zones of the metallogenetic belts. Here its deposits are connected not only with the potassium granitoids intruding in the late stages of the tectono-magmatic cycle, but often also with the essentially sodium granitoids confined to the earlier stages of the cycle and revealing a genetical connection with basic magmas. Owing to this, molybdenum is one of the most typical metals for the interior zones of the metallogenetic belts, probably even more typical than for the exterior zones which will be described below. In the interior zones it forms deposits of the disseminated, stock-work and vein type and often manifests a close local and genetical connection with copper deposits.

The occurrence of tungsten in metallogenetic provinces of this type is much rarer and in much smaller quantities, and it is found almost exclusively in connection with potassium granitoids of the late stages of the tectono-magmatic cycle. It forms usually small vein deposits with wolframite or scheelite, and contact-metasomatic scheelite deposits. Bismuth does not form independent deposits but is sometimes found as a mineral admixture in deposits of other metals (gold, copper), and only seldom in quantities making its extraction as a by-product worth while (Japan). Finally in most of the metallogenetic provinces of this type tin is practically absent and gives insignificant concentrations only in separate regions (Norway, Italy, Japan).

For the metallogenetic provinces of this type sulphur must be referred to as the most characteristic mineralizer, entering both into the sulphides and some of the sulphates, which are important vein minerals (baryte, gypsum, alunite). In the deposits of iron, titanium and phosphoric acid also play an important rôle. Boron, carbon dioxide and, particularly fluorine are much less important as mineralizers.

Metallogenetic provinces entering into the exterior zones of the metallogenetic belts are most widely represented by deposits genetically connected with acid potassium granitoids. Among them

must be cited in the first place the deposits of tin and partly of tungsten, which are the most characteristic deposits of the provinces of this type. It is sufficient to mention the huge belt of tin and tungsten deposits occurring in the Mesozoic folded zone of Eastern Asia and the identical deposits of the Erzgebirge, of Cornwall and the Pyrenees Peninsula in Western Europe. Sometimes, in connection with them are also encountered concentrations of economic value of bismuth and molybdenum, but for the latter the interior zones of the metallogenetic belts play, anyhow, a more important rôle.

For the metallogenetic provinces of this type lead and zinc deposits are also rather characteristic. They are usually younger than the tin-tungsten deposits, and contrary to the interior zones of the metallogenetic belts, they are not represented by sulphide lodes, but either by vein deposits (Erzgebirge, Harz), or by replacement deposits in limestones (the region of the Rhine, Silesia, Transbaikal), or by contact-metasomatic deposits (the Far East, etc.). In provinces of this type occur also deposits of economic value of mercury, antimony and arsenic.

The rôle of copper, iron and gold is subject to great variations, and according to the development of the deposits of these metals, as well as to some other features, it would be rational to subdivide the metallogenetic provinces of the exterior zones into two sub-types, which can be designated as the West European and East Asiatic. In the West European sub-type of mineralization, the rôle of tin-tungsten, and particularly of the molybdenum mineralization is, on the whole, lower, than in the East Asiatic subtype, where deposits of economic value of copper are practically absent. Of much greater importance is the silver-lead-zinc mineralization. Peculiar siderite and hematite hydrothermal deposits of iron are very characteristic of the West European subtype of mineralization, whereas in the East Asiatic subtype the magmatogene deposits of iron are almost absent, except for the scanty and small contact-metasomatic deposits of magnetite.

Of great importance is the difference between the two subtypes of mineralization of the exterior zones, with regard to mineralizers and the composition of the vein minerals. The most characteristic vein mineral for the East Asiatic subtype is quartz, often encountered together with large quantities of tourmaline and ferrous chlorites. Boron is one of the most characteristic mineralizers in this subtype of metallogenetic province, and involves the occurrence of considerable quantities of tourmaline in the deposits of almost all the metals (gold, molybdenum, tin, tungsten, zinc, lead, etc.). Besides the hydrothermal deposits a considerable mineralization due to boron is also observed in the contact-metasomatic deposits. Carbonates and fluorite play quite a secondary rôle as vein minerals in the East Asiatic subtype of mineralization, and barite is practically absent.

In the West European subtype of mineralization quartz remains one of the most important vein minerals, but here it is often hornfels or chalcedony-like. The distribution of tourmaline is much more restricted and is confined to tin-tungsten deposits. Instead, the different carbonates, barite, and fluorite, are extremely widespread vein minerals of ore deposits, and the latter two often form independent deposits of great economic value. It is no wonder, that Europe, on the whole, plays a leading part in the production of barite, witherite, and fluorite. The presence of iron chiefly in the form of oxygen compounds (hematite, siderite), large quantities of carbonates and sulphates among the vein minerals, witness the important rôle of oxygen as one of the mineralizers.

Such typical metals of the basic and ultra-basic magmas as platinum, chromium, and titanium are practically absent in both subtypes of mineralization of the exterior zones.

Thus, notwithstanding essential features of likeness, the metallogenetic provinces of the West European and the East Asiatic subtype differ greatly, which does not allow them to be united into one group. These differences become evident not only in the complex of characteristic metals, but also in the composition of mineralizers and vein minerals.

Of great interest is the behaviour of iron in different types of metallogenetic provinces, depending on the composition of the mineralizers. In the metallogenetic provinces of the interior zones, the main mass of iron partakes in the formation of the pyrites and of the magnetite, titano-magnetite and apatite-magnetite ores (mineralizers: sulphur, titanium, phosphorus and partly oxygen). In the

provinces of the West European subtype iron forms mainly hematite and siderite ores (mineralizers: oxygen, carbon dioxide). Finally, in the provinces of the East Asiatic subtype iron hardly gives rise to deposits of economic value, but enters in geochemically enormous quantities into the composition of ferrous tourmalines (mineralizer: boron), and partly into that of the ferrous chlorites.

As already mentioned, the processes of sedimentation do not cause very sharp geochemical differences between the different types of orogenic zones. Considering the series of sedimentary rocks proper, it is perhaps possible to point out the rather important rôle of the carbonate (and volcanic) facies in the interior zones of the metallogenetic belts and of the terrigenous facies in their exterior zones. However, the distribution of some types of sedimentary deposit needs special attention. Thus, for instance, it can be seen that the sedimentary deposits of manganese and the deposits of geosynclinal bauxites show a definite trend toward those metallogenetic provinces which have been designated above as the interior zones of metallogenetic belts. On the contrary, the sedimentary deposits of the minerals of strontium (celestite, strontianite) show a trend toward the metallogenetic provinces of the West European subtype (Germany, Great Britain). Such a regularity indicates, that besides climatic and facial conditions of those basins in which these deposits were formed, the presence of primary sources of these metals was of great importance and is closely related to magmatic activity and to processes of magmatogene mineralization. In any case, before the definition of metallogenetic characteristics of any given province, this purely empirical regularity must be borne in mind.

The attempt of the author to subdivide the orogenic zones into separate geochemical types, according to the magmatic activity and the process of mineralization connected with it, represents only a first approximate scheme. Nevertheless, it distinctly shows that not all the orogenic zones possess similar geochemical characteristics, and that they can be sub-divided, according to the latter, at least into three different types.

О ГЕОХИМИЧЕСКИХ ТИПАХ ОРОГЕНИЧЕСКИХ ЗОН

Ю. А. БИЛИБИН

Геохимический облик геосинклинальных и возникающих из них орогенических зон создается тремя главнейшими группами геологических процессов:

а) процессами седиментации.

б) процессами магматической деятельности.

в) процессами магматогенной минерализации.

Процессы седиментации создают наибольшие по об'ему массы горных пород, однако, при этом не возникает столь резких геохимических различий, которые могли бы быть положены в основу выделения различных геохимических типов орогенических зон. Процессы собственно магматической деятельности обычно создают несколько меньшие по об'ему массы горных пород, но геохимические различия между отдельными орогеническими зонами выражены здесь значительно более резко. Наконец, процессы магматогенной минерализации создают сравнительно очень небольшие по об'ему массы, но с наиболее четко выраженными геохимическими различиями. Так как возникающие при этом минеральные месторождения являются об'ектами промышленной разработки, геохимические различия между ними в различных типах орогенических зон представляют наибольший интерес. Эти различия не являются независимыми, но вытекают из геохимических различий между магматическими породами, с рассмотрения которых поэтому приходится начинать.

Для геосинклинальных и возникающих из них орогенических зон считаются характерными, с одной стороны, излияния основных лав спилитовой формации в подготовительный или геосинклинальный перилд развития, которые часто сопровождаются или чередуются с интрузиями основных и ультраосновных магм. Последние дают характерные для орогенических зон офиолитовые пояса значительной протяженности. С другой стороны, для периода окончательного осушения геосинклинали и превращения ее в ороген характерно значительное развитие крупных батолитов кислых, существенно калиевых гранитоидов. Эти два типа магматических проявлений, достаточно различные геохимически, считаются характерными вообще для всех геосинклинально-орогенных зон.

Ближайшее рассмотрение показывает, что в подавляющем большинстве орогенических зон действительно присутствуют оба эти типа магматических проявлений, однако, в очень неравномерном количественном развитии. В тех орогенических зонах, где очень сильно проявлены излияния основных лав спилитовой формаций и интрузии основных и ультраосновных магм, калиевые гранитоиды представлены обычно в ослабленном развитии. Наоборот, там, где последние представлены очень широко, в очень ослабленном развитии представлены основные и ультраосновные магмы периода геосинклинального развития. Эти количественные различия часто выражены настолько резко, что могут служить основанием для того, чтобы рассматривать эти две категории геосинклинально-орогенных зон, как два различные геохимические их типа.

Это различие было впервые отмечено покойным русским академиков С. Смирновым для мезокайнозойского складчатого пояса, опоясывающего Тихий океан. В этом складчатом и, вместе с тем, металлогеническом поясе академик Смирнов различал две зоны: 1) внешнюю, ближайшую к континенту, сформированную в течение мезозоя, с широким развитием калиевых

гранитоидов и свойственной им металлогении при крайне слабом развитии основных и ультра-основных магм, и 2) более молодую внутреннюю, блифайшую к океану, сформированную в период, охватывающий конец мезозоя и весь кайнозой, с очень широким развитием средних, основный и ультраосновных магм при явно ослабленном развитии калиевых гранитоидов.

Рассмотрение других складчатых и металлогенических поясов показывает, что такое разделение на два геохимических типа, с известным приближением, приложимо также и к ним. В частности, к типу внутренних зон металлогенических поясов могут быть отнесены Скандинавский металлогенический пояс (каледониды Норвегии), мезокайнозойская зона Средиземноморского пояса (юг Европы, Балканский полуостров, Турция, Закавказье, Иран), восточный склон Урала, Саянский металлогенический пояс (Сибирь) и некоторые другие. К геохимическому типу внешних зон, кроме мезозойской складчатой зоны Тихо-океанского пояса, должны быть относены варисские складчатые структуры Средней и Западной Европы, западный склон Урала и др. Следует оговориться, что под внутренними и внешними зонами мы понимаем не части одной геосинкинамли, а самостоятельные геосин-клинальные зоны, разновременно и последовательно формирующиеся в пределах более крупных структурных единиц, определяемых нами, как геосинклинальные и металлогени-ческие пояса. Не входя в рассмотрение взаимоотношений внешних и внутренних зон во времени и пространстве, мы будем в дальнейшем понимать под этими терминами лишь опреде-ленные геохимические типы орогенических зон. Попытаемся дать их сравнительную геохи-мическую характеристику, сначала в отношении магматизма, а потом в отношении металлогении.

Для внутренних зон металлогенических поясов исключительно характерны обширные излияния основных магм в подготовительный период развития геосинклинали. Обычно они представлены спилитами, порфиритами (андезитами), нередко также более кислыми породами типа альбитофиров и кварцевых альбитофиров. Это хорошо известная спилитовая магматическая формация. Таковы докембрийские и нижнепалеозойские лавовые излияния Норвегии, силурийские и девонские лавы восточного склона Урала, кембрийские лавы Саянского пояса, мезокайнозойские лавовые излияния южной и юго-восточной Европы и юго-западной Азии (Турция, Кавказ, Иран), а также Тихоокеанского побережья Азии и Америки.

Для всех орогенических зон с обильными излияниями лав спилитовой формации характерно очень широкое развитие основных и ультраосновных магм и их диференциатов также в интрузивной форме. Обычно эти интрузии чередуются с поверхностными излияниями и часто бывают связаны с фазами складчатости, временно прерывающими, но не прекра-щающими полностью процесс геосинклинального развития. Сюда относятся, прежде всего, гипербазитовые интрузии, часто образующие офиолитовые пояса значительного протяжения. Таков, например, Средиземноморский офиолитовый пояс, протягивающийся с некоторыми перерывами от южной Европы до островов Малайского архипелага, Уральский офиолитовый пояс, Саянский и многие другие. Помимо гипербазитов, в тех же орогенических зонах обычно развиты интрузивные комплексы, представленные гдавным образом основными и средней кислотности породами при подчиненном развитии кислых пород. Для последних в боль-шинстве случаев характерно заметное, а иногда очень резкое преобладание натрия над калием, благодаря чему среди них часто играют существенную роль породы типа трондьемитов или плагиогранитов. К подобным интрузивным комплексам, относятся, прежде всего, известные анортозит-чарнокитовая и опдалит-трондьемитовая группы Норвегии, многочисленные габбровые, диоритовые и плагиогранитные интрузии Урала, Кузнецкого Алатау, Саяна, Балкан, Малой Азии, Кавказа, Тихоокеанского побережья Америки и др. Во всех этих случаях обнаруживается тесная генетическая связь кислых (существенно натриевых) пород с породами более основными.

Обычные богатые калием гранитоиды, не связанные генетически с основными породами,

наиболее характерны для тех этапов тектоно-магматического цикла, с которыми связано окончательное осушение геосинклинали и превращение ее в ороген. В орогенических зонах рассматриваемого типа эти гранитоиды обычно представлены в заметно ослабленной степени по сравнению с орогеническими зонами иных типов. Они значительно более узко локализованы во времени и в пространстве, чем основные интрузии и их диференциаты. В то время как последние бывают распространены на всей площади орогенов рассматриваемого типа и повторяются неоднократно на протяжении длительных отрезков геологического времени, интрузии калиевых гранитоидов обычно отвечают одной-двум последним фазам складчатости и локализуются преимущественно в отдельных, наиболее глубоких прогибах, дольше других участков орогена сохранявших свою лабильность.

Очень характерный пример в этом отношении дает Уральская складчатая зона. Здесь интрузия основных и ультраосновных магм в сопровождении их более кислых, существенно натриевых диференциатов, повторялись многократно на протяжении силура, девона и нижнего карбона, захватив всю площадь складчатой зоны Восточного Урала. Интрузии калиевых гранитоидов, не связанные генетически с основными магмами, проявились лишь в верхнем карбоне и только в определенном, наиболее грубоком прогибе вдоль восточного склона Урала.

Для этого типа огоренических зон очень характерны проявления, кроме основных и кислых, также щелочных магм. Среди последних принято выделять два ряда—калиевый и натриевый. Необходимо отметить, что различия между ними наиболее отчетливы в породах более основных—щелочных габброидах и базальтоидах. В более лейкократовых породах эти различия сильно сглаживаются, и щелочные породы близкие к эвтектическим составам (фонолиты, нефелиновые сиениты), нередко идентичны в обоих рядах.

В орогенах типа внутренних зон встречаются проявления как натриевых, так и калиевых щелочных магм. Однако, последние являются более характерными. В эффузивных фациях они представлены лейцитовыми породами, калиевыми трахитами, фонолитами и другими богатыми калием породами, в интрузивных фациях—шонкинитами, монцонитами, псевдолейцитовыми породами, калиевыми фоятами и др. Лейцитовые лавы и сопровождающие их другие богатые калием эффузивные породы исключительно характерны для последних этапов вулканической деятельности Средиземноморского орогена. Сюда относятся лейцитовые лавы Италии, Югославии, Турции, Кавказа, Ирана, островов Малайского архипелага (Ява, Борнео, Целебес и др.). Эти богатые калием щелочные породы прослеживаются здесь настолько закономерно, что их приходится считать не менее характерными для Средиземноморского орогена, чем его офиолитовый пояс.

Во внутренней зоне Тихоокеанского пояса не только калиевые, но вообще щелочные магмы представлены значительно слабее. Вероятнее всего об'яснять это тем, что магматизм внутренней зоны Тихоокеанского пояса в большинстве ее районов еще не достиг в своей эволюции стадии проявления щелочных магм. В пользу такого предположения говорит интенсивный современный вулканизм этой зоны с излиянием главным образом основных и средних магм, которые предшествуют излияниям щелочных магм, если судить по примеру Средиземноморского и других поясов. Достойно быть отмеченным, что в некоторых изолированных прогибах, расположенных несколько в стороне от внутренней зоны Тихоокеанского пояса и испытавших более быструю эволюцию магматизма, излияния основных и средних магм уже сменились излияниями лейцитовых лав (восточная окраина Большого Хингана в Манчжурии, бассейн Большого Анюя). Единичные находки лейцитовых лав отмечаются и в некоторых других участках внутренней зоны Тихоокеанского пояса (Н. Зеландия, Калифорния, Антарктика и др.).

В пределах Скандинавского, Уральского и Саянского поясов щелочные породы представлены преимущественно нефелиновыми сиенитами, но возможно, что лейцитовые породы Шотландии и Северного Казахстана (Ишим) связаны с эволюцией магматизма именно этих

поясов. Для Урала может быть также отмечено интенсивное проявление калиевых лав повышенной щелочности (трахиты) в верхнем лудлоу.

Иной является характеристика магматизма для другого типа орогенических зон, определенного нами выше, как внешние зоны металлогенических поясов. В подготовительный период развития геосинклиналей здесь также имеют место поверхностные излияния основных и средних лав, иногда с них кислыми натриевыми диференциатами. Однако, в количественном отношении разница с первым типом орогенических зон разительная. Здесь основные эффузии подготовительного периода приурочены к узко ограниченным периодам времени, значительно более узко локализованы в своем площадном распространении и играют резко подчиненную роль в общей мощности стратиграфического разреза. Таковы варисская складчатая зона Центральной и Западной Европы, варисская складчатая зона Монголии, западный склон Урала, мезозойская складчатая зона Восточной Азии и др. В громадных по протяженности участках последней эффузивы подготовительного периода практически отсутствуют и поверхностная вулканическая деятельность здесь начинается в основном уже после превращения геосинклинали в ороген.

В полном соответствии с этим находится и слабое развитие основных и ульраосновных интрузий во внешних зонах металлогенических поясов. Они никогда не образуют здесь сколько-нибудь протяженных поясов, но встречаются лишь в отдельных, ограниченных по площади, районах. В мезозойской складчатой зоне Восточной Азии они почти совершенно отсутствуют, если не считать небольших гипабиссальных интрузий, возникших уже в условиях орогена, в очень поздние стадии эволюции последнего.

Наоборот, интрузии калиевых гранитоидов являются исключительно характерными для орогенических зон этого типа. Они пользуются здесь очень широким площадным распространением и возникают в связи с многочисленными последовательными фазами складчатости. Таковы многочисленные варисские гранитоидные интрузии Центральной и Западной Европы, варисские гранитоидные интрузии Монголии и, особенно, мезозойские гранитоидные интрузии Восточной Азии.

Богатые калием щелочные породы для орогенических зон этого типа менее характерны, чем для зон первого типа. Иногда встречаются нефелиновые сиениты. Но наиболее характерными из щелочных пород являются, пожалуй, меланократовые щелочные породы натриевого ряда типа эссекситов, тешенитов, кринанитов и др. Они возникают в поздние этапы эволюции магматизма этих орогенических зон, преимущественно в их форландах, хотя нередко встречаются и в пределах самих орогенов. Таковы карбоновые тешениты и родственные им породы Шотландии, тешенитовые интрузии западного склона Урала, Монголии и исключительно широко распространенные верхнемезозойские (до кайнозойских) тешениты северо-восточной Азии.

Таким образом, хотя в выделенных нами двух типах орогенических зон качественно представлены более или менее одни и те же группы магматических пород, как эффузивных, так и интрузивных, но их количественное развитие является резко различным. В то время как в первом типе (внутренние зоны металлогенических поясов) резко преобладают в эффузивных и интрузивных проявлениях основные, ультраосновные и средней кислотности магмы и отчасти щелочные калиевые, во втором типе (внешние зоны металлогенических поясов) резко преобладают калиевые гранитоиды и отчасти щелочные натриевые породы. Наибольшая напряженность магматической деятельности в первом типе орогенических зон отвечает в целом геосинклинальному периоду развития, включая сюда и временно прерывающие его фазы складчатости, во втором типе—периоду превращения геосинклинали в ороген и последующего орогенного развития.

Если количественные различия в характере магматической деятельности в двух выделенных типах орогенических зон выступают достаточно отчетливо, то еще более четко прослеживаются различия в их магматогенной минерализации.

Для внутренних зон металлогенических поясов особенно характерны магматогенные месторождения, генетически связанные с основными, ультраосновными и средней кислотности магмами и отчасти с их более кислыми, существенно натриевыми диференциатами. Наиболее характерными металлами являются платина, хром, титан, никель, железо, медь, отчасти молибден, кобальт, цинк, свинец, ртуть, мышьяк. Наоборот, типичные металлы кислых калиевых магм—олово и висмут являются очень мало характерными. Наибольшее промышленное значение имеют месторождение и гистеромагматические, контактово-метасоматические, вкрапленные руды, колчеданные залежи и лишь отчасти жильные месторождения.

К месторождениям орогенических зон этого типа относятся месторождения хромитов и крупнейшие магнетитовые месторождения. Очень характерны для этого типа минерализации медноникелевые колчеданы. Еще более характерными и широко распространенными являются медноколчеданные и сероколчеданные месторождения, являющиеся наиболее типичной металлогенической чертой всех орогенических зон этого типа. Свинцово-цинковые месторождения в орогенах этого типа также в большинстве представлены колчеданными залежами и лишь в резко подчиненном количестве жильными месторождениями. В то же время, для меди, одного из наиболее характерных металлов в орогенах этого типа, очень велика роль и других типов месторождений; вкрапленных руд, штокверковых, жильных.

Распределение благородных металлов (золото, серебро) по типам месторождений подвержено значительным колебаниям в различных металлогенических провинциях этого типа. Наоборот, для молодых металлогенических зон этого типа (мезокайнозойская зона Средиземноморского пояса и, особенно, кайнозойская зона Тихоокеанского пояса) исключительно характерны мощные концентрации золота и серебра в эпитермальных месторождениях (Трансильвания, Турция, Н. Зеландия, Япония, С. и Ю. Америка). Нельзя умолчать о приуроченности к этим же металлогеническим зонам типичных близповерхностных месторождений ртути и мышьяка (Италия, Югославия, Западные штаты США и др.).

Очень интересно поведение в металлогенических провинциях этого типа тех металлов, которые считаются характерными для кислых калиевых магм, то есть, молибдена, вольфрама, висмута, олова. Из них молибден является наиболее характерным для провинций, входящих во внутренние зоны металлогенических поясов. Его месторождения бывают здесь связаны не только с калиевыми гранитоидами, проявляющимися в поздние этапы тектона-магматического цикла, но нередко и с существенно натриевыми гранитоидами, приуроченными к более ранним этапам цикла и обнаруживающими генетическую связь с основными магмами. Благодаря этому, молибден является одним из характерных металлов для внутренних зон металлогенический поясов, пожалуй, даже более характерным, чем для характеризуемых ниже внешних зон. Во внутренних зонах он дает месторождения вкрапленного, штокверкового и жильного типа и часто обнаруживает тесную пространственную и генетическую связи с месторождениями меди.

Вольфрам встречается в металлогенических провинциях этого типа значительно реже и в несравненно меньших количествах, почти исключительно в связи с калиевыми гранитоидами поздних этапов тектономагиматческого цикла. Он дает обычно небольшие жильные месторождения с вольфрамитом или шеелитом и контактово-метасоматические шеелитовые местрождения.

Висмут не дает самостоятельных месторождений, но иногда встречается в качестве минералогической примеси в месторождениях других металлов (золота, медь), лишь в редких случаях в количествах, делающих рентабельным его попутное извлечение (Япония). Наконец, олово в большинстве металлогенических провинций этого типа практическп отсутствует и лишь в единичных районах (Норвегия, Италия, Япония) дает очень незначительные концентрации.

с

Из минерализаторов для металлогенических провинций этого типа наиболее характерна сера, входящая в состав как сульфидов, так и некоторых сульфатов, являющихся существенными в качестве жильных минералов (барит, гипс, алунит). В месторождение железа существенную роль играют также титан и фосфорная кислота. Бор, углекислота и, особенно, фтор играют в качетсве минерализаторов значительно меньшую роль.

В металлогенических провинциях, входящих во внешние зоны металлогенических поясов, наиболее широко представлены месторождения, генетически связанные с кислыми калиевыми гранитоидами. Среди них необходимо прежде всего отметить месторождения олова и отчасти вольфрама, являющиеся наиболее характерными месторождениями в провинциях этого типа. Достаточно упомянуть грандиозный пояс оловянных и вольфрамовых месторождений мезозойской складчатой зоны Восточной Азии и такие же иместорождения Рудных Гор, Корнуолла и Пиренейского полуострова в Западной Европе. Иногда в связи с ними встречаются также промышленные концентрации висмута и молибдена, но для последнего внутренние зоны металлогенических поясов имеют все таки большее значение.

Довольно характерны для металлогенических провинций этого типа также свинцовоцинковые месторождения. По возрасту они обычно являются более молодыми, чем оловянновольфрамовые, и, в отличие от внутренних зон металлогенических поясов, представлены не колчеданными залежами, а либо жильными месторождениями (Рудные Горы, Гарц), либо месторождениями замещения в известняках (Рейнская область, Силезия, Забайкалье), либо контактово-метасоматическими (Дальний Восток и др.). В провинциях этого типа встречаются также промышленные месторождения ртути, сурьмы, мышьяка.

Роль меди, железа и золота сильно варьирует, и по развитию месторождений этих металлов, а также по некоторым другим признакам целесообразно разделить металлогенические провинции внешних зон на два подтипа, которые могут быть обозначены, как западноевропейский и восточноазиатский. Для западноевропейского подтипа минерализации роль оловянно-вольфрамового и, особенно, молибденового оруденения в целом ниже, чем для восточноазиатского подтипа. Резко снижена также роль золотого оруденения, зато промышленное значение медного оруденения много выше, чем в восточноазиатском подтипе, где промышленные медные месторождения практически отсутствуют. Также значительно больше роль серебро-свинцово-цинкового оруденения. Своеобразные сидеритовые и гематитовые гидротермальные месторождения железа очень характерны для западноевропейского типа минерализации, в то время как в восточноазиатском типе магматогенные месторождения железа почти отсутствуют, если не считать немногочисленных и очень небольших по масштабу контактово-метасоматических месторождений магнетита.

Очень существенной является разница между двумя подтипами минерализации внешних зон в отношении минерализаторов и состава жильных минералов. В восточноазиатском подтипе наиболее характерным жильным минералом является кварц, наряду с которым часто встречаются в значительных количествах также турмалин и железистые хлориты. Бор является одним из наиболее характерных минерализаторов в этом подтипе металлогенических провинций, обуславливая появление существенных количеств турмалина в месторождениях почти всех металлов (золото, молибден, олово, вольфрам, цинк, свинец и др.). Помимо гидротермальных месторождений, существенная минерализация бором наблюдается и в контактово-метсоматических месторождениях. Карбонаты и флюорит в качестве жильных минералов играют в восточноазиатском подтипе минерализации резко подчиненную роль, а барит практически отсутствует.

В западноевропейском подтипе минерализации кварц остается одним из главных жильных минералов, но нередко является роговиковым или халцедоновидным. Турмалин имеет значительно меньшее распространение и приурочен лишь к оловянно-вольфрамовым месторождениям. Зато различные карбонаты, барит и флюорит являются исключительно широко

распространенными жильными минералами рудных месторождений, а барит и флюорит нередко дают и самостоятельные месторождения крупного промышленного значения. Не случайно, что Европа в целом занимает ведущее место по добыче барита, витерита и флюорита. Присутствие железа преимущественно в форме кислородных соединений (гематит, сидерит), большое участие карбонатов и сульфатов в составе жильных минералов указывают на существенную роль кислорода в качестве одного из минерализаторов.

Что касается таких типичных металлов основных и ультраосновных магм, как платина, хром, титан, то они практически отсутствуют в обоих подтипах минерализации внешних зон.

Таким образом, несмотря на значительные черты сходства, металлогенические провинции западноевропейского и восточноазиатского подтипов обладают и существенными различиями, не позволяющими об'единять их в одну группу. Эти различия проявляются не только в комплексе характерных металлов, но также в составе минерализаторов и жильных минералов.

Очень интересным является поведение железа в различных типах металлогенических провинций в зависимости от состава минерализаторов. В металлогенических провинциях внутренних зон железо в подавляющей массе входит в состав колчеданов и магнетитовых, титаномагнетитовых и апатит-магнетитовых руд (минерализаторы сера, титан, фосфор, отчасти кислород). В провинциях западноевропейского подтипа железо дает главным образом гематитовые и сидеритовые руды (минерализаторы кислород, углекислота). Наконец, в провинциях восточноазиатского подтипа железо почти не дает промышленных месторождений, но в геохимически громадных количествах входит в состав железистых турмалинов (минерализатор бор) и отчасти железистых хлоритов.

Процессы седиментации, как уже отмечалось, не создают очень резких геохимических различий между различными типами орогенических зон. Если говорить о толщах собственно осадочных пород, то можно, пожалуй, отметить лишь несколько повышенную роль карбонатных (и вулканогенных) фаций во внутренних зонах металлогенических поясов и терригенных фаций в их внешних зонах. Однако, распределение некоторых типов осадочных месторождений невольно обращает на себя внимание. Так, например, бросается в глаза, что осадочные месторождения марганца и месторождения геосинклинальных бокситов определенно тяготеют к тем металлогеническим провинциям, которые были нами определены, как внутренние зоны металлогенических поясов. Наоборот, осадочные месторождения минералов стронция (целестин, стронцианит) тяготеют к металлогеническим провинциям западноевропейского подтипа (Германия, Великобритания). Такая закономерность говорит о том, что помимо климатической обстановки и фациальных условий тех бассейнов, в которых эти месторождения образовались, очень существенную роль играло наличие первичных источников питания этими металлами, которые приходится искать в магматической деятельности и процессах магматогенной минерализации. Во всяком случае, эту чисто эмпирическую закономерность не бесполезно иметь в виду при установлении металлогенической характеристики тех или иных провинций.

Сделанная автором попытка разделить орогенические зоны на отдельные геохимические тилы по характеру магматической деятельности и связанной с нею минерализации является лишь первой приближенной схемой. Тем не менее, она отчетливо показывает, что не все орогенические зоны обладают сходной геохимической характеристикой, и что они могут быть разделены по этому признаку по меньшей мере на три типа.

SERPENTINE AND TALC EQUILIBRIA

By N. L. BOWEN and O. F. TUTTLE

U.S.A.

ABSTRACT

An experimental investigation has been made of the equilibrium relations of talc and serpentine with the anhydrous phases forsterite, enstatite, periclase and silica at pressures of water vapour up to 30,000lbs. per sq. in. and temperatures up to 900°C. Pressure-temperature curves have been determined for the successive four-phase equilibria: serpentine + brucite $\rightleftharpoons$ forsterite + vapour, serpentine $\rightleftharpoons$ talc + forsterite + vapour, talc + forsterite $\rightleftharpoons$ enstatite + vapour, talc $\rightleftharpoons$ enstatite + quartz + vapour, brucite $\rightleftharpoons$ periclase + vapour.

No liquid phase (magma) is formed in any composition up to the highest temperatures and pressures at which the investigations were carried out. Pure magnesian serpentine can exist only up to a temperature of approximately 500°, the upper limit of its stability being only slightly affected by pressure.

[Full publication as " The System MgO—SiO₂—H₂O " in *Bulletin of the Geological Society of America*, vol. lx, 1949, pp. 439–460.]

DISCUSSION

J. P. MARBLE enquired in what form the silica appeared which was produced in these reactions (i.e., quartz, tridymite or cristobalite).

P. NIGGLI wished to know whether the serpentine phase was chrysotile or antigorite.

TH. VOGT asked if an iron component would lower the transformation temperatures between the chemical equilibria which had been demonstrated and how much. This question was one of some interest for the natural rocks with some iron.

N. L. BOWEN, in reply, said that at the lower temperatures the silica was always in the form of cristobalite but at the higher temperatures it always appeared as quartz which is, of course, the stable form in all the conditions in which they worked. The serpentine phase was always chrysotile in all cases where it could be determined. The serpentine formed by serpentinization of olivine was, however, obtained in very small quantity and it was not possible to determine its character. In the case of serpentinization of olivine the temperature is lowered some 80°C. by the presence of about 7 per cent FeO in the olivine. They were unable to induce serpentinization of hortonolite from the Bushveldt at any temperature.

AN ALTERNATIVE TO THE HYDROTHERMAL THEORY OF ORE GENESIS

By J. S. BROWN

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ABSTRACT

The validity of the hydrothermal theory is questioned and a geological and chemical basis offered for a substitute. Geological support for the alternative is based on (1) mineral paragenesis and (2) zoning. Paragenesis is suggestively related to specific gravity; lighter minerals escape first and heavier ones later, indicating gravity stratification in the source magma. Zoning is related similarly to volatility, the more volatile substances travelling farthest, the least volatile being deposited deepest. This implies that the major method of transfer is as vapour.

Chemical support for the theory is found in the principles of blast furnace smelting with the well-known differentiation of dissimilar substances into layers such as slag, matte, and speiss. The heavy sulphide layers are shown to be analogous to probable sulphide ore magmas.

The existing concept of a single source magma for all elements of an ore sequence is held to be incompatible with metallurgical principles, and separate sources are deduced for silicates (pegmatites), oxides (iron ores), and sulphides. The sulphide magma is believed to constitute a widespread sheet resting on a peridotite basement at a depth of 40 to 60 kilometres.

INTRODUCTION

FOR nearly half a century the study of ore deposits has been dominated by the hydrothermal theory. It is assumed under this concept that most primary ores originate in connection with igneous activity, as a result of the differentiation of a rock melt. In its final stages the process is supposed to generate a mother liquor or " ore magma " rich in whatever metallic or non-metallic ingredients may combine to form an ore deposit. The magma supposedly is rich in silica. The whole mélange is assumed to be unified by being dissolved in a great volume of water, and in the final crystallization of the magma this water is expelled upward to regions where falling temperature and pressure compel it to deposit its mineral load. The mechanics and chemistry of this process have been discussed at greatest length, perhaps, by Graton (1940).

In spite of the obvious relation of many ore deposits to igneous action, however, the hydrothermalists fail to present any clear, logical, or unified concept of the processes involved. They disagree as to whether the ore fluid was acid or alkaline, whether it was dilute or highly concentrated, whether it rose as liquid or as gas, whether it came from the upper or the lower portion of the related intrusive, and many other details as well.

There have been occasional nonconformists who have expressed disbelief in the hydrothermal theory or cast doubt on certain of its aspects, but they have received little attention, perhaps mainly because they failed to offer any constructive substitute. Prominent among English dissenters has been Arthur Holmes (1937, 1938) who seems to have been inspired by his predecessor, J. W. Gregory (1928).

Gregory based his doubts on the field evidence as to the occurrence of lead ores, so often found in essentially similar deposits either near or far from areas of past igneous activity. Holmes supplemented this with data on the radioactive nature of various types of lead. In the United States Basil Prescott expressed the scepticism of certain practising geologists by the conclusion that the field evidence failed completely to substantiate the basic assumptions of the hydrothermal theory (1946). My own experience and research on similar deposits led me to the same conclusion (1947). Unlike previous dissenters, I pursued the matter to the point where I feel justified in presenting an entirely new hypothesis. This seems to me to preserve most of the virtues of the hydrothermal theory, which are

chiefly superficial, and to resolve many of its ambiguities, which are fundamental. This hypothesis, which will be set forth in detail in a forthcoming book (1948), is based primarily on logical deduction and analogy from certain related lines of geological evidence, the first of which is the field of mineral paragenesis.

SPECIFIC GRAVITY AND PARAGENESIS

Strangely, although geologists differ so widely as to the nature of the ore magma and its manner of escape, they agree substantially as to the facts of mineral paragenesis. Lindgren (1936) summarized it as follows:

" The interesting fact soon becomes apparent that practically the same paragenesis holds for contact-metamorphic, hypothermal, mesothermal and epithermal deposits."

Surely any such well established law must stem from some fundamental uniformity in the nature of the ore magma and the conditions of its escape, yet no rational explanation has ever been advanced.

It has, indeed, been pointed out that paragenesis in sulphide ores seems to bear some relation to the atomic weight of the anion or metal component, metals of least atomic weight generally appearing earliest in the sequence (Bandy, 1940). However, in oxide or silicate ores the conditions are greatly confused or even reversed. In my pursuit of this problem it developed that a more likely basis of control might be plain weight or specific gravity rather than atomic weight, as illustrated by the following tabulation for sulphide ores.

Paragenetic Sequence	Specific Gravity		Atomic Weight of Metal
Pyrite (FeS_2)	5·02	...	55·84
Pyrrhotite (Fe_nS_{n+1})	4·70	...	55·84
Sphalerite (ZnS)	4·08	...	65·38
Chalcopyrite ($CuFeS_2$)	4·28	...	63·57
Enargite ($3Cu_2S \cdot As_2S_3$)	4·45	...	63·57
Tennantite ($4Cu_2S \cdot As_2S_3$)	4·62	...	63·57
Stibnite (Sb_2S_3)	4·57	...	121·76
Galena (PbS)	7·57	...	207·22
Boulangerite ($5PbS \cdot 2Sb_2S_3$)	6·15	...	(121·76–207·22)
Argentite (Ag_2S)	7·32	...	107·88
Cinnabar (HgS)	8·10	...	200·61
Bismuth (Native)	9·75	...	209·00
Silver (Native)	10·50	...	107·88
Gold (Native)	19·33	...	197·20

The paragenetic sequence is a generalization but is commonly accepted with only minor variations such as the occasional reversal of the positions of sphalerite and chalcopyrite, or galena and certain lead-antimony sulphides. The correspondence to specific gravity is closer than to atomic weight, especially in the heavier elements.

METALLURGICAL ANALOGIES

Note that this tabulated sequence can be divided very naturally into three parts; (1) an upper portion mainly of pyritic sulphide and zinc sulphide, (2) a middle zone comprising arsenides and antimonial sulphides, (3) a lower zone dominated by galena and precious metals.

Metallurgists will perceive at once a striking relation between this and certain elementary principles of the art of smelting as depicted in Fig. 1.

In the blast furnace smelting of copper and lead several strata form in the melt:

(1) A slag containing all the silicates and oxides;

(2) A matte composed of pyritic sulphides and zinc sulphide;

(3) A speiss containing nickel, iron, arsenic, and antimony with copper, zinc and lead;

(4) In lead smelting, due to reducing reactions deliberately incited, a fourth layer of molten lead which collects nearly all the precious metals. Unreduced lead sulphide sometimes occurs in small volume above this layer.

SP GR	SLAG	M P
3.0 – 3.5	SILICATES AND OXIDES	DEG C 1150 ±
5.0 – 5.5	MATTE FE CU ZN SULPHIDES	900 ±
5.7 – 6.3	SPEISS FE₂CU,NI,AS,SB,S	600 ±
7.0 – 7.5	PBS–(CU₂S) AU AG BI	800 ±

FIG. 1.—*Blast furnace segregation of sulphides.*

The remarkable resemblance of this series to the paragenetic sequence is obvious. Can it be that this suggests the true nature of an ore magma, and that paragenesis results from the successive liberation of the components from the top downward? The idea is refreshingly concrete as compared to the vague inferences of the hydrothermal theory. It provides no room, however, for the aqueous vehicle of transport. What, then, would be the probable manner of escape? It is not likely that it would be by fluid injection, since the magmatic ingredients have segregated at depth because of their excessive weight. Some other means of transport seems essential, and naturally the principle of volatile transfer or vaporization at once suggests itself. The pertinent data regarding the volatility of common sulphides may be summarized as follows:

Volatility of sulphides (Mellor, 1922–37*)

Mineral	Melting Pt.	Volatility
Realgar	320°C.	In absence of air " sublimes far below red heat."
Stibnite	546°C.	Distils readily with air excluded.
Cinnabar	...	Volatilizes without melting, 580°C.
Pyrite, arsenopyrite, chalcopyrite	...	In air, dissociate at 675°, 690°, 600°C. No data for air excluded.
Argentite	840°C.	" Sublimes readily in quartz vessels." Dissociates perceptibly at 950° in air.
Galena	1,130°C.	Volatile below M.P.; often deposited in blast furnaces.
Sphalerite	1,645°C.	Strong sublimation 1,000°–1,200°C.
Chalcocite	1,130°C.	Data lacking. Dissociation and transformations occur.
Pyrrhotite	1,175°C.	Low dissociation pressure at M.P.
Bismuth	271°C.	Vapour pressure 32 mm. at 1,119°.
Silver	960°C.	,, 1 mm. at 1,200°.
Gold	1,063°C.	,, 1 mm. at 1,500°.

*Data regarding volatility taken generally from J. W. Mellor.

The sulphides of arsenic, antimony and mercury volatilize readily at comparatively low metallurgical temperatures, and galena and sphalerite at a moderately higher range. The pyritic sulphides when heated in air and at atmospheric pressure tend to dissociate into sulphur and a lower grade sulphide, but there is evidence tending to suggest that, under pressure and in the absence of air, they might volatilize as entities at temperatures not far above their dissociation points. The transport of sulphides as simple mineral vapors, therefore, seems to be a reasonable possibility. If this actually occurs in nature it should be susceptible of a certain measure of proof by comparison with another well-known geological principle, that of mineral zoning. A comparison between volatility and the zonal succession is presented in the following table.

Volatility and Zoning

Volatility Scale	Zonal Succession (following Emmons, 1926)
Realgar	Cinnabar (and marcasite).
Stibnite	Stibnite (with galena and gold).
Cinnabar	Gold tellurides; argentite, realgar, stibnite.
Enargite?	Pyrite (sparse).
Tennantite	Argentite, arsenopyrite.
Pyrite?	Galena, sphalerite, chalcopyrite.
Arsenopyrite?	Tetrahedrite, enargite, tennantite.
Chalcopyrite?	Chalcopyrite, pyrite, pyrrhotite (main zone).
Argentite, galena	Gold, pyrite, arsenopyrite.
Sphalerite, Pyrrhotite	Quartz and sparse sulphides, bismuth, tourmaline, etc.
Bismuth	
Silver and gold	

In this table the most volatile substances are listed at the top of the volatility scale, those which travel farthest from igneous sources at the top of the zonal column. The parallelism is fairly close. The most volatile sulphides, those of arsenic, antimony and mercury travel farthest. The pyritic sulphides, and especially pyrrhotite, which volatilize with difficulty are deposited near or even within intrusive masses. Most gold, silver and bismuth are deep-seated. Minerals of intermediate volatility such as galena and sphalerite and especially the arsenical and antimonial sulphides or speisses typify the mesothermal or intermediate range. Gold and silver occur to some extent in the intermediate range, perhaps because they attach themselves to volatile elements such as sulphur, selenium or tellurium for the journey and then dissociate on deposition. Previous attempts to explain the enigma of mineral zoning on the basis of solubility in aqueous solutions have been so at variance with the facts that even strong advocates of the hydrothermal theory have confessed failure. Cinnabar, one of the least soluble of all sulphides, invariably travels farthest, while the pyritic sulphides, which are most soluble, are generally deposited first. Surely volatility offers a far more rational explanation of the facts than solubility.

THE SULPHIDE ORE MAGMA

If it is admitted that sulphide ores may originate by volatilization from a concentrated magma which has been gravitationally stratified, what can be inferred as to the probable location and extent of such a magma? In this connection let us consider the broader features of the composition of the earth's crust as illustrated in Fig. 2. Ignoring superficial sediments, it is generally agreed that the immediate crust to a depth of perhaps 25 kilometers has the average composition of granite, the sial layer. Beneath this, with a thickness of perhaps 35 kilometers is a heavier gabbroic or basaltic layer. This, in turn, rests on a shell perhaps 1,500 kilometers or more in thickness of peridotite, which is still heavier and also has a melting point some 200 to 400 degrees higher than that of the basaltic or granitic shells. It is commonly agreed that these shells owe their arrangement to gravitational segregation which most geologists attribute to cooling from a state of fusion. It is clear that, in this process, the peridotite should solidify first, and this would seem to provide the logical base for the location of a primordial sulphide source stratum, at a depth of roughly 60 kilometers or 37 miles.

The thickness of this possible source stratum is problematical, but assuming only that amounts of sulphides corresponding to those presently known to exist in the accessible portions of the earth's

crust may have accumulated gravitatively at depth, the thickness of the lead layer should be about two feet and the entire sulphide series nearly 300 feet. Assuming that the small amounts of sulphides now found in average igneous rocks constitute merely the residue held in solution in a silicate slag and that the sulphide stratum may have segregated with something like the efficiency of metallurgical process of recovery, that is from 75 to 95 per cent, the total thickness might well be from 1,200 to 1,500 feet and the lead layer alone could easily amount to 40 feet.

The fact that mineral paragenesis follows much the same laws the world over, implies that the magmatic source is very similar in nature throughout the world and suggests, therefore, that the sulphide magma may be worldwide in extent. There are some grounds, however, for believing that there may be an important differentiation between the continental areas and the deep oceanic basins and that the sulphide magma may be restricted largely to the continents.

The fact that individual mining districts differ, some yielding predominantly copper, some lead, others gold, etc., implies either that only a particular portion of the sulphide zone was yielding mineral

THICKNESS	CRUSTAL SHELLS	SP. GR.
25 KM	GRANITE	2.7
35 KM	BASALT	3.0
1200 KM	PERIDOTITE	3.3 OR MORE

FIG. 2.—*Constitution of the earth's crust (after Hess).*

vapors at the time these deposits were formed, or else that erosion has exposed them to that particular horizon of deposition. The observed fact that certain types of mineral deposits seem to characterize various eras of geologic time may very well be a corollary of the stratified arrangement of the magmatic source. Thus, at an early stage in the earth's cooling, when the entire sulphide series presumably was molten, it was primarily the topmost or pyritic layer which yielded mineral vapors. Pyritic ores thus characterize the late pre-Cambrian and early Cambrian eras. When the pyritic matte had become largely frozen, it was primarily the underlying but still readily molten speiss and lead layers that supplied mineral vapors. Thus the Mesozoic is the great era for the formation of lead the world over.

GANGUE MINERALS IN THE METAL SEQUENCE

If a source magma thus consists almost entirely of metallic mineral components, what is the proper explanation of the abundant gangue minerals which commonly accompany the ores, and are so often interpreted as paralleling or interrupting the paragenetic succession? If there is any validity to the hypothesis proposed, it is obvious that these substances have nothing to do with the ore magma, but are simply materials which the ore vapors have displaced in their ascent and which have been re-deposited along the way. In some cases this process of displacement or alteration and redeposition long has been recognized and admitted, as in the sericitization or carbonitization of the wall rocks of veins. But there has also been a strong tendency under the hydrothermal theory to ascribe to many non-metallic substances a magmatic origin identical with that of the ore minerals. This assumption that quartz and carbonates, carbonates and sulphides, sulphides and oxides must all originate in a single ore magma and be deposited in a continuous sequence by a uniform carrier seems very unreasonable. How can acid and alkali be derived from a single source at the same time, or chemically and metallurgically incompatible substances accumulate harmoniously in a common reservoir?

THE SILICATE AND OXIDE ORES

Sulphides, of course, do not comprise the whole range of ore minerals, in spite of their predominance. Two additional classes of importance have been avoided thus far in order to concentrate attention upon the significance of density and volatility in relation to paragenesis and zoning.

First of all, it is generally agreed that, in many instances, the earliest phase of ore formation is a process of silication or silicate formation. This often takes the form of pegmatite injection and may be accompanied by valuable ore minerals such as apatite, mica, wolframite, beryl, mica and cassiterite. The relations of pegmatites to granitic intrusives are so close and so clearly transitional in many cases that they are commonly accepted as constituting an end phase of granitic consolidation. For this reason the effort often has been made to interpret sulphide ore formation as merely an extension of the pegmatitic process, but this has generally failed to meet satisfactorily the field evidence that pegmatite emplacement usually was complete long before sulphide introduction occurred.

Similarly, with the important group of oxide ores, particularly the iron ores including magnetite, hematite and ilmenite, the field and microscopic evidence usually is clear that these tend to follow silicates and to be followed in turn by sulphides. The oxide ores frequently mark the culmination of a process once popularly designated as contact metamorphism in which intense silication in such form
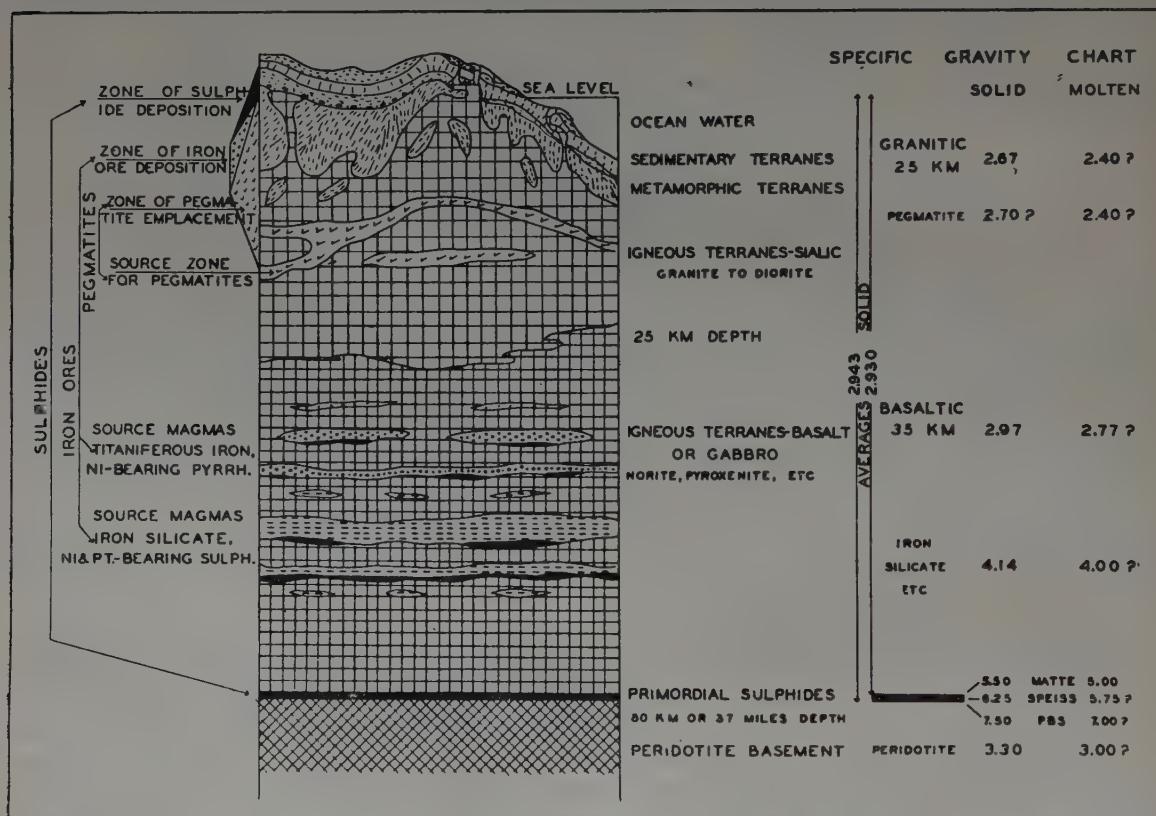
FIG. 3.—*Relations of the various source magmas and their zones of deposition.*

as garnetization, epidotization, etc., ended in the deposition of iron ores and may have been followed by a minor wave of sulphides. Thus the full paragenetic succession is well established as: (1) silicates; (2) oxides; (3) sulphides; a working principle long used but never adequately explained.

In Fig. 3 an attempt is made to fit these additional classes of ores into a reasonable position harmonizing with the facts of field geology and also with the conception of a deep-seated sulphide source layer.

Fig. 3 presents a detailed interpretation of the composition of the earth's crust and the probable sources of ores in amplification of the essentials given in Fig. 2. At the top is a zone 5 to 10 kilometers thick of sedimentary and metamorphic rocks, the area in which ores commonly are deposited. Beneath

is the granitic or sialic layer, which is the source of the great bulk of our predominant intrusives, the granite family and its allied effusives. Since pegmatites are virtually an end stage of granitic intrusion it seems reasonable to suggest that they are the product of an independent type of magma, ore magma in some instances, which is generated at a high level. This is inherently of low specific gravity and hence probably is emplaced mainly by fluid injection. The high position of this pegmatitic magma in the rock column assures it naturally of being the first of the ore-making series to be emplaced in any area where igneous activity is subsiding and ore materials are being liberated in order from the top downward.

Beneath the granitic layer is the basaltic stratum, distinguished by its fairly low silica content and high iron and magnesia. This seems to be the natural place to seek the source magmas of primary iron ores, and it is suggested that stratified sheets highly enriched in iron such as are known at various places in association with great basic intrusive sheets actually constitute the probable source of most primary oxides of iron and titanium. Their position thus falls appropriately at a level intermediate between the source magmas of pegmatites and sulphides. In the process of successive liberation from the top downward they fit naturally into the proper time interval following pegmatites and related silicates but preceding sulphides. The exact manner of emplacement is left open, but it may include fluid injection in some cases and volatilization in others.

THE FUNCTION OF WATER IN ORE FORMATION

We have now reached the final phase of the problem, the rôle of water in ore formation. It might be inferred by this time that the author is completely atheistic and would deny that water has any part in the ore forming process, but this is by no means true. The low solubility of all ore substances in water seems to indicate that it is unreasonable to invoke water as the primary means of transport from the magma. It also seems wholly incompatible with chemical and metallurgical experience to believe that water can accumulate in appreciable volume at the depths where ore magmas probably are generated under the present hypothesis, or even at the depths commonly accepted to-day by most hydrothermalists, which tend to be well beyond the deepest zones uncovered by erosion, or necessarily many miles below the original surface. It is also inconsistent with the known facts as to the occurrence of water, which are tabulated herewith.

Water Content of Rocks

Clay and alluvium	5 to 50 per cent.
Soft sandstone	5 to 25 ,,
Limestone (porous)	5 to 15 ,,
Shale	5 ,,
Slate, quartzite, marble	1 to 2 ,,
Igneous rocks, crystalline	Under 1 ,,

It seems obvious that water exists chiefly at the earth's surface, in the oceans, lakes and rivers, and that the amount contained in ordinary rocks decreases directly with their depth from the surface and their degree of consolidation and in all crystalline rocks is comparatively insignificant. These facts are wholly in accord with the known lightness and volatility of water. Wherever it is carried down to any appreciable depth in the earth's crust by entrainment, it should soon be squeezed out, or expelled as steam and returned toward its home at the surface.

Wherever ore vapors rise into the water-saturated crust, however, water becomes at once a vital reagent of precipitation and, for short distances, of transportation. It also doubtless aids immeasurably in the disposition of the substances replaced, either by rendering them volatile at low temperatures or by carrying them away in solution. In this process hydrothermal solutions undoubtedly are generated in great volumes, and this doubtless accounts for the extraordinary hold of the hydrothermal theory upon the imagination of geologists. At the scene of deposition its evidences are often overwhelming. This, however, is hardly justification for attributing equal importance to aqueous solutions at the depths where ores are generated.

It is suggested, therefore, that geologists give serious thought to revising their concept of the origin of ores by eliminating water as a factor of any importance in the accumulation or primary transport of ore substances, and by restricting it to a very vital role in precipitation at the site of deposition.

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DISCUSSION

E. L. BRUCE: The theories of the formation of ore deposits have reached such an unsatisfactory and static position that it is a matter of much interest to have a contribution such as this especially one from a person who not only is concerned with theoretical considerations but one who has achieved outstanding success in the discovery and development of bodies of ore. I hesitate to attempt to discuss the paper without having had an opportunity to read it but there are certain aspects of it with which I cannot fully agree. It might be pointed out that if the transfer of elements occurs under supercritical conditions the distinction between solutions and gases disappears. Mr. Brown has pointed out that the table of zonal arrangement of ores is incomplete. I should like to add that it also shows gold in a position which Mr. Brown would consider as indicating a minimum amount of transfer from the parent magma. Yet field and laboratory investigations show that in most gold deposits the gold is a late constituent, and that it occurs at so great a distance from the source that the igneous rocks formed from its source magma are commonly never to be found.

K. C. DUNHAM: Mr. Brown is to be congratulated on reminding geologists that large-scale experiments involving silicates and sulphides are carried out every day in smelting operations, and that a body of physico-chemical data on the subject exists. It may well be that a stratiform arrangement, corresponding generally with the three layers (silicate-matte-speiss) existed in the primordial earth. The transfer of material from the sulphide layer to the highest parts of the crustal shell where sulphide ore deposits are now found represents a fundamental problem. At first volatility seems even less competent to explain the facts than the now traditional hydrothermal theory, and I shall be interested to read how Mr. Brown reconciles a temperature of volatilization of 1,130°C. for galena with the world-wide presence of this mineral in deposits of the Mississippi Valley type, whose temperature of formation can have been little above 100°C.

W. NIEUWENKAMP: What is the relation of this conception to those of Vogt and V. M. Goldschmidt who also had the comparison with the blast furnace constantly in mind?

J. S. BROWN (in reply): These comments scarcely call for any definite reply. They present questions of importance which have been considered and discussed at length in the author's book which sets forth these ideas in detail. In the specific case of the question as to how the matte layer may be disposed of to pave the way for volatilization of speisses, this could be either by the freezing of the matte, permitting it to fracture and provide avenues of escape, or by its lateral displacement due to changes of load due to erosion and sedimentation.

QUIMISMO DE ALGUNOS GRANITOS DE PONTEVEDRA (ESPAÑA)

By G. M. CARDOSO and I. P. PONDALL

Spain

ABSTRACT

Se estudia la mancha de granito de biotita de Porriño. Salvatierra y Puenteareas de 190 km²., limitada al sur por el rio Miño, al N y E por granito de dos micas y al W por gneis de horblenda y gneis normal.

Granito porfidíco, con biotita. La manchá está constituida por un granito de tipo ácido con feldespato rosado; en él solo se observan muy escasos filoncillos aplíticos, y por otro menos ácido con horblenda y feldespato blanco enclavado dentro del área del primero.

Entre los minerales accesorios se destacan el apatito, esfen a, circón, ortita.

Para el estudio de la diferenciacion se han hecho varios análisis químicos. Basándose en ellos se formulan los números de Niggli siguientes:

	si	al	fm	c	alk
Aplita Bugasín	462	44·5	11·5	5·5	38·3
Granito de biotita Porriño	382	43·5	10·0	3·5	43·0
Id. Id. Pesqueiras	347	44·5	14·5	11·0	30·0
Granito de horblenda Cabreiras ...	254	33·5	24·0	14·0	28·5
Gabarro Cabreiras	182	29·5	33·0	17·0	20·5

Estos números demuestran que se trata de granitos procedentes da la diferenciación magmática en la serie calco-alcalina del tipo normal de P. Niggli.

DISCUSSION

J. L. AMORÓS: El Profesor Cardoso se ha referido en su trabájo a diferencias de interpretación sobre la edad y origen de las formaciones graníticas del N.W. de España, entre los geologos españoles y portugueses. ¿Podría el Prof. Cardoso hacer una breve exposicíon de las principales diferencias arriba indicadas?

G. M. CARDOSO (in reply): En efecto hay disparidad de criterios entre los geólogos españoles y los portugueses y entre los portugueses mismos con la tendencia de la escuela de Cotelo Neiva a considerar una misma edad para todos y la de los españoles que con ligeras variantes suponen tres periodos: el más antiguo antecámbrico de granito normal o gneísico muy alterado, el caledoniano de dos micas y el posterior heránico de biotita, al cual hay que atribuir de amerdo con los geólogos españoles del final del siglo XIX el granito de Pamíro.

THE DISTRIBUTION OF BARIUM IN THE ALKALINE ROCKS AND FENITES OF ALNÖ ISLAND

By HARRY VON ECKERMANN

Sweden

ABSTRACT

In connection with a comprehensive petrological study of the alkaline rocks and the surrounding fenites of Alnö Island more than 120 rock analyses were made. In most cases the content of BaO was determined. A subsequent separate study of the rock minerals is still in progress, and many complete analyses of minerals are already available.

Although not complete, the data now on hand allow of a preliminary review of the distribution of BaO in the alkaline rocks of magmatic origin and in the surrounding syenitic and nephelinized fenites. They disclose a considerable migration of barium ions from the intrusive liquids into the metasomatically metamorphosed wall rock. They illustrate also the concentration of barium in the residual solutions, viz., the leucocratic and carbonatitic rocks rich in potash; this partly being due to gravitational separation of mafic minerals poor in barium.

The ultimate concentration of barium occurs as barite veins, which were discovered during the years of the last world war. They have been mined since 1943 and met the demand of the Swedish market when the import of barite failed.

IN the course of a recent comprehensive petrological study of the alkaline rocks and their surrounding fenites of Alnö Island 124 rock analyses were made and in most cases the content of BaO was determined. A subsequent separate study of the rock minerals is still in progress but 30 complete analyses of minerals are already available. Although not complete, the data now on hand may serve to shed some additional light on the distribution of barium in alkaline rocks.

Rankama in his paper on the geochemical differentiation in the earth's crust refers barium to a group of elements, called by him the granitophile elements, which tend to concentrate in the outermost parts of the earth's crust. He presents, too, a compilation of the determinations by previous authors of the BaO content of different rocks, and calls attention to the strong enrichment in the rapakivi

TABLE I

BaO Percentage

	Minimum	Maximum	Average	Number of Analyses
Migmatites:				
Gneiss-granite	0·01	0·01	0·01	2
Schists	0·06	0·06	0·06	1
Fenites:				
Melanocratic	Trace	0·07	0·03	3
Mesocratic	0·07	0·18	0·12	2
Leucocratic	0·04	0·46	0·25	4
Alkaline Intrusives:				
Melanocratic	0·08	0·35	0·20	4
Mesocratic	0·05	0·33	0·27	4
Leucocratic	0·25	0·62	0·47	4
Sövites	0·07	0·29	0·18	2
Dike-Rocks:				
Alnöites	0·08	0·25	0·17	3
Ouachitites	0·26	0·27	0·27	3
Nepheline-Porphyries	0·08	0·36	0·27	3
Beforsites (dolomitic carbonatites)	0·00	0·61	0·24	6
Alvikites (calcitic carbonatites)	0·03	0·77	0·27	7

granites and its further increase in the Paleozoic and Mesozoic granites as well as in the Tertiary granophyre. The alkaline rocks, however, are not represented and the closest approach is an average value of $0\cdot2$ per cent given by von Engelhardt for syenites.

The new determinations of the BaO content of the rocks are given in Table I. Comparing those of the Archaean migmatite with the gneissose granites of Rankama's compilation the magnitude is of the same order, although slightly lower. Within the fenites a very strong enrichment is noted which seems to reach higher top values in proportion to the increasing feldspar and nepheline contents. The same is the case in the magmatic intrusive rocks where still higher minimum, maximum and average values are registered. The BaO-content of the carbonatitic rocks of " abyssic " character, so called sövites, which accompany the main magmatic intrusive, is equivalent to that of the mesocratic intrusive rocks.

If we turn to the dike rocks of hypabyssal character we do not find the same regularity of distribution between leucocratic and melanocratic rocks. The maximum values may be said to constitute a rising series, but not so the minimum or the average ones. This becomes understandable when one bears in mind that while the " abyssal " rocks are all samples of contemporaneous equilibria at one and the same intrusion level, now uncovered by erosion, the dike rocks of cone-sheet character, although sampled at the very same level have travelled different and far greater distances in shorter time than the more slowly rising magma column of the central conduit. The fractures of the wall rocks, caused by an explosive shattering due to a sudden increase in internal CO_2 pressure, were probably very rapidly filled by the magmatic liquid forced out from the respective cone-sheet foci. The examination of the resulting rocks has led to the deduction that in most cases very little alteration has taken place during their " mise en place," bar some carbonization. Of very great interest is therefore the almost constant average value, $0\cdot27$ per cent BaO, of all the dike rocks except the most femic ones, the alnöites. It not only confirms the rapid consolidation of the dikes but suggests, too, a corresponding percentage of BaO in the main intrusive at the depths of the cone-sheet foci.

If we now examine the hitherto established distribution of BaO in the minerals, given in Table II, the absence of any barium in the nepheline and the maximum values in the case of the soda-orthoclase immediately attracts our attention. The nephelines are both samples from the fenitic rocks, that is to say represent the product of nephelinization " in situ " of the wall rocks of the magmatic conduit.

Of the feldspars two samples derive from the fenite; the one of the higher BaO percentage from the inner fenite boundary, the other one from about the middle of the zone of nephelinization. Nothing is, consequently, known as yet about the barium content of the nepheline of the intrusive rock; its apparent increase in proportion to the nepheline and feldspar content may in this case, too, be due to the feldspar alone. As, however, the magmatic liquid was the carrier of the barium it seems reasonable to expect its distribution over both nepheline and feldspar.

TABLE II

BaO Percentage

	Intrusive Siliceous rocks	Sövites	Fenites	Alnöite
Nepheline	...	...	0·00	...
"	...	...	0·00	...
Soda-Orthoclase	1·62	...	0·37	...
"	1·20	...	0·72	...
Biotite	...	...	...	0·53
"	...	0·71	...	...
"	...	0·55	...	...
"	...	0·55	...	...
Melanite	...	...	0·06	...
Barkevikitic Hornblende	0·04	...	...	0·04
Aegirine-Augite	0·06	0·03	0·00	...
"	0·02	0·02	0·00	...
"	...	0·00	...	...

I have shown elsewhere that during the process of fenitization potash migrated from the intrusive liquid simultaneously with the formation of nepheline. As far as can be judged from the few analyses now available, a considerable diadochic replacement of K by Ba did take place in the orthoclase lattice but none in that of the nepheline. This may suggest that the potash of the latter mineral derives from the original potash of the fenitized migmatite, while that of the soda-orthoclase migrated, wholly or partly, from the central alkaline intrusive. Until this suggestion, as well as the absence or presence of barium in the various nephelines, is definitely proved by further analyses, any speculation about the reason for this selective replacement is premature. It may be noted, however, that synthetic Ba-nepheline produced by Weyberg in 1909 did not agree satisfactorily with the formula $R_2Al_2Si_2O_8$.

Next to the soda-orthoclase the biotite contains the largest percentage of BaO. Of the four analyses hitherto executed, three refer to biotite from sövites and one, the lowest, to the biotite phenocrysts of an alnöite. As the fenite generally does not contain any biotite within the zones where an increase of BaO has been established, the mineral in question is of no use when studying the migration of barium into the fenite. On the other hand, a future study of the distribution of BaO over the biotites of the different intrusive rocks may furnish some interesting data.

A mineral which will have to be investigated as a possible bearer of some of the barium enrichment of the fenite is the apatite, the increase of which is conspicuous during the last stages of fenitization. At present two analyses only, both of sövite-apatites, are available. The one of low barium content occurs in a sövite poor in apatite, while the one of high content is sampled from a sövite very rich in apatite, up to 25 per cent and more. If this connection is accidental or not will have to be shown by further analyses.

As might have been expected the femic minerals melanite, pyroxene and barkevikitic hornblende all show very low barium contents. This applies to the minerals of intrusive rocks and fenitic rocks alike.

Finally, a few words may be said about the large-scale concentrations of barium discovered during the years of the last war at a critical time when the Swedish import from Germany was cut off. The barium occurs as barite veins hundreds of metres long and 2-3 metres wide. When they were first looked for, the search was based on the new tectonic picture arising from the re-survey of Alnö and on the assumption that barite concentrations, if any, should be expected to occur in those zones of weakness where the post-magmatic activity may be supposed to have survived the longest.

When the first dike was discovered an old botanic hobby provided an unforeseen " short cut " by which not only could the direction of the veins be followed above the covering drift, but new dikes discovered, too. A bush with red berries, *Lonicera xylosteum*, was observed to grow above the outcrops of the veins where it thrives on the sulphurous soil, but not on the barium. This was verified both by analysis and by the occurrence of the bush along the outcrops of pyritic sövite dikes, too.

The barite dikes have been mined at a rate of about 4,000 tons a year. Their total lateral and vertical extension is at present unknown, but they do not seem to run to any great depths. About two thirds of the veins consist of almost pure barite, 99·5 per cent, while the remaining third is composed of marginal alternating zones of barite, calcite and two types of fluorite, one of a normal violet fluorescence and the other of a bright yellow one. The SrO content of the pure barite is 0·06—0·03 per cent only.

DISCUSSION

E. S. Larsen, jr.: In the crystallization and differentiation of basaltic magmas, barium tends to be concentrated in the residual liquid during the early stages. On the crystallization of biotite and potash feldspar barium is greatly concentrated in the early material to crystallize, thus impoverishing the residual liquid in barium. The last residual liquid is nearly free of barium. This is well illustrated in the rocks of the Highwood Mountains, Montana, where sanidine crystals are strongly zoned with cores that contain over 6 per cent of BaO and outer zones that are nearly free of BaO.

Barium may be nearly lacking in the deuteric and early hydrothermal minerals, but may be concentrated in late hydrothermal solutions.

RELATION BETWEEN ORE FORMING PROCESSES AND INTRUSIVE ROCKS

By I. F. GRIGORIEV

U.S.S.R.

ABSTRACT

Admitting a telethermal migration of ore fluids for some types of deposits, attention should be drawn to some facts indicating a close relation between the change of the ore mineralization and the alteration of wall rocks and the geological conditions of the intrusion and the cooling of the igneous mass.

In some cases the places of the separation of ore solutions can be supposed to be nearer than it is generally assumed. Among such factors are the following:

(*a*) Change of the character of ore mineralization in deposits, connected with small porphyry intrusions, for portions within the intrusion as well as for portions among intruded rocks.

(*b*) Specific dikes, small intrusives and ore deposits in marginal granodioritic portions of large granite batholiths are distinct from dikes and ore deposits in the main granitic mass.

(*c*) Various types of the hydrothermal alteration of intruded rocks adjacent to the same granitoid mass are represented in some places by skarns, and in others by hydrothermally altered quartzites with aluminous silicates. The influence of various enclosing rocks may indicate a close origin and nearby separation of ore-bearing fluids of a different composition.

D

PHASE RULE AND GEOCHEMICAL
MOBILITY OF ELEMENTS

By D. S. KORZHINSKY

U.S.S.R.

ABSTRACT

An equilibrium assemblage of minerals composed of n components, depends on $n + 2$ independent factors. A part of them are factors of extensity (the content of some components), others are factors of intensity (temperature, pressure, concentration of some components in percolating solutions). The maximum number p of minerals in assemblages, formed under given conditions, is equal to the number of independent factors of extensity. Other $n + 2 - p$ factors are independent factors of intensity, in accordance with Gibbs' Phase Rule. By applying systematically this rule to rocks, we may establish that some components under given conditions are " perfectly mobile," their concentrations in solution being independent factors, whereas others are " inert," their concentrations in solution being functions of their content in the rock.

The geochemical mobility of elements and oxides depends on the activity of solutions, temperature and depth, and is connected mainly with solubility in natural solutions.

The decreasing mobility series for high temperature processes of the most deep-seated gneiss complexes is: H_2O, CO_2, S, SO_3, Cl, K_2O, Na_2O, F, CaO, O_2, Fe, P_2O_5, BaO, MgO, SiO_2, Al_2O_3, TiO_2.

For high-temperature processes near the surface it is: H_2O; CO_2, S, K_2O, Na_2O, O_2, MgO, Fe, CaO, SiO_2, P_2O_5, Al_2O_3, TiO_2; and for low-temperature processes near the surface: H_2O, CO_2, S, K_2O, Na_2O, O_2, Cu, SiO_2, CaO, MgO, Fe, P_2O_5, Al_2O_3, TiO_2.

ONE of the most fundamental tasks of geochemistry, as defined by Russian academicians V. I. Vernadsky and A. E. Fersman, is the study of geochemical migration of elements. Therefore the geochemical mobility, that is the ability of elements and oxides to migrate (to be transported) in the course of natural processes of formation and alteration of rocks and ores, is one of their important geochemical properties. The mobility is extremely different for different components and is dependent mainly on the solubility of a given component in natural aqueous solutions, the presence of which is necessary for the formation of minerals, at any rate of silicates. Moreover, the ability of a component to diffuse and the ability to percolate with the solution through the pores of rocks (filtration effect) are also of importance.

In studying the geochemical mobility of elements particular importance should be attached to a systematic analysis of the regularities in mineral association on the basis of the phase rule.

As it is known, Gibbs' Phase Rule expresses the relation between the number of components n, the number of phases p, and the number of freedom degrees f in an equilibrium system:

$$f + p = n + 2.$$

V. Goldschmidt (1911) was the first to apply the phase rule to mineral associations in a simplified form of " the mineralogical phase rule " ($p \leqslant n$). Since that time the phase rule gained general acceptance in petrography and was used by many authors to establish the stability or instability of mineral associations in rock and as a basis for a graphical analysis and representation of equilibrium mineral associations of rocks.

In addition, the phase rule was proved to be applicable in establishing the relative mobility of elements, a discussion of which will be proceeded to.

The physico-chemical parameters, or values characteristic of the state of a system, may be divided into intensive and extensive ones. The former do not depend either on the mass of separate phases in the system or on the ratio of their masses, whereas the latter do. The intensity factors comprise the

temperature, pressure and concentration of components in phases. The extensity factors include the heat content of the system, its volume, and the amount of each component in the system.

Gibbs' Phase Rule considers only the intensity parameters. The number of independent intensity parameters, i.e., the number of degrees of freedom, f, according to this rule is $n + 2 - p$. What is then the total number of independent intensive and extensive parameters in the system $(f_i + f_e)$? If we determine the system with the aid of all its independent intensity parameters, $f_i - n + 2 - p$, and add the masses of each phase, i.e., p of the independent extensity parameters, the system will be perfectly determined, the total number of independent parameters being $f_i + f_e = (n + 2 - p) + p = n + 2$.

Thus the total number of independent parameters, both intensive and extensive, of the system does not depend on the number of its phases but only on the number of its components; viz., the former exceeds the latter by two.

In the case of an abstract physico-chemical system it makes no difference which of the parameters would be considered as independent, and which as dependent ones, only the total number of independent parameters being unquestioned. We may assume to be independent only the extensive factors, determining the system by the masses of each of the K components, the total volume and heat content of the system, i.e., by the $n + 2$ extensive parameters. Then all the remaining extensive and intensive parameters would be functions of the independent parameters used. But we may substitute a part of the extensive factors by corresponding intensive ones; that is, instead of the volume of the system its pressure may be used; instead of the heat content of the system, its temperature; instead of the amount of a component in the system, either its concentration in one of the phases or the activity or the chemical potential of this component in the system. The number of independent intensity factors f_i however, cannot exceed the number $n + 2 - p$, that is:

$$f_i + f_e = n + 2$$
$$f_i \leqslant n + 2 - p$$
$$p \leqslant f_e \leqslant n + 2$$

In concrete systems, however, the state is determined by quite definite factors, for which reason the division of parameters into independent and dependent ones ceases to be arbitrary. Some of the parameters are determined by the external conditions of the process or by the initial state of the system. Such external parameters, independent of the physico-chemical properties of a given system, certainly are always independent equilibrium factors. The values of the dependent parameters are fixed at points depending both on the physico-chemical properties of a given system and on the external factors. In order to understand the natural process which has brought about the present state of equilibrium, it is very essential to establish the extensive or intensive nature of the external factors. To achieve this, the phase rule may be helpful.

In the processes of mineral and rock formation in the earth's crust, due to a possible change in volume and heat diffusion, it is not the extensive parameters, heat content and volume but the intensive parameters, viz., temperature and pressure that are external factors as suggested by V. Goldschmidt. Hence the number of independent intensive parameters for each equilibrium association decreases by two, as a result of which Goldschmidt's " mineralogical phase rule " $(p \leqslant n)$ is obtained. The practice of applying the phase rule to rocks has fully justified Goldschmidt's assumption considering temperature and pressure as independent factors of mineral formation.

As to composition, in a closed system it is obviously determined by extensive factors only, viz., by the amount of components in the initial state. But the case is possible when it will be only for a part of the components that their amount in the final equilibrium state of the system will be dependent on the initial amount, whereas for the rest the amount will depend on the concentrations of these components in the supplied solution or, in general, will be determined by the activity of these components in the external medium. Consequently, just as the heat conditions of a system may be determined in some cases by the constant heat content (of a thermally isolated system), and in other cases, by the temperature of the surrounding medium—so will be the amount of a given component determined in some cases by the initial content, and in others, by its activity in the surrounding medium.

Hence it is a case of semi-opened systems, which are closed for some components and opened for others.

In the laboratory we have to do with a half-opened system for instance, when igniting nonvolatile substances in an open crucible. The amount of these substances in the crucible is not changed, whereas the oxygen and nitrogen content for equilibrium states will depend not on their initial amount in the crucible but on their pressure in the atmosphere and on the nature and content of nonvolatiles in the crucible. Another example is presented by membrane (osmotic) equilibrium. In natural processes of rock formation and alteration half-opened systems are common, due to the fact that some of the components are poorly soluble in the aqueous solutions affecting the rocks and hence are not displaced, while others are readily soluble, easily diffuse through the solution or readily percolate along with the solution through the wall rocks; therefore their activity in the rock should correspond to that of the incoming solution.

The components which do not change their content in the course of processes of a given type will be termed " fully inert " during these processes. The components whose content does not depend on the initial content but is determined by the activity in the external medium (e.g., in the incoming solutions) will be termed " fully mobile " during a given type of processes. These are two extreme ideal cases. But the subsequent deductions are applicable also to such more natural cases when the inert components may somewhat change their content, however not to such a degree that the deviation from the ideal inertness should result in a change of the type or number of phases in the system considered.

Applying the phase rule to mineral associations we are justified in considering as phases only minerals, although in the formation and alteration of rocks, at least of silicate rocks, a part was doubtless played by some solutions afterwards removed.

Rejecting two degrees of freedom related to temperature and pressure, we obtain the phase rule in the following form:

$$p = n - f_c$$

where f_c designates the number of independent (free) concentrations of the components. The number of minerals in an equilibrium association is thus equal to the number of components minus the number of free concentrations. However, in concrete cases only a part, f_{cm}, of these free concentrations changes really independently, representing external concentrations of fully mobile components. Another part, f_{ci}, is the number of degrees of freedom of those possible variations in the composition of minerals which depend on the variations in the contents of inert components and therefore are not independent. Systems of minerals are possible in which the composition is constant and does not permit any variations with regard to the inert components considered ($f_{ci} = 0$). For such systems the number of free concentrations f_c is equal to the number of fully mobile components, n_m, whereas the number of minerals of a constant composition in an equilibrium association is equal to the number of inert components n_i:

$$n = n_i + n_m; \; f_c = n_m; \; p = n - f_c = n_i; \; n_m = n - p$$

The number of mobile components is obviously equal to the difference between the total number of components and the number of minerals. Thus in the extreme case of a complete absence of solid solutions, after having determined the number of minerals in the equilibrium association and the number of elements present in them, we might establish what number of these elements behaved in a fully mobile manner during the formation of the rock.

In the general case of the presence of minerals of a variable composition we have:

$$f_c > n_m; \; p < n_i; \; n_m < n - p; \; p = n_i - f_{ci},$$

i.e., the maximum number of minerals in an equilibrium association is equal to the number of inert components and does not depend on the number of fully mobile components.

As may be seen from the above formulae, in using the phase rule one may neglect the presence of fully mobile components in the system, simultaneously decreasing both the number of components and the number of free concentrations. In a similar way, in a graphic analysis of the dependence of

the mineralogical composition on the chemical composition it would be sufficient to consider only the inert components if a set of rocks or ores is studied, which have been formed under constant conditions of temperature, pressure and concentration of the incoming solutions. As a matter of fact, independent variations of the composition are possible only with respect to the inert components, and the mineralogical composition is a function of the ratio of inert components, the above-mentioned external conditions being constant.

The contrast, just considered, of the behaviour of inert and of fully mobile components should be displayed not only in ideal half-open systems, fully closed for the inert components. This contrast should exist also in more natural systems in which all the components are mobile but in a various degree. Due to the differential mobility of the components, a complete equalization of the activity in the rock with that in the incoming solutions at first occurs only for the most mobile components. For the less mobile components while displacement may take place, still there are retained variations in the initial composition which are not related to differences in the composition of the incoming solutions. Generally speaking, if a system ceases to be ideally closed for inert components and their content begins to change, this brings about at first only a change of the relative amounts of phases and a change in their composition, without producing any changes in the number of phases or their type, i.e., without disturbing the inertness of the behaviour of such components in the sense considered above.

A special case is presented by a fully mobile component, the concentration of which is maintained by the external conditions on a level of saturation which makes possible a precipitation of this component in the pure state or in combination with other fully mobile components. Such a concentration is obviously not a free but a fixed one, and hence the possible appearance of an additional phase does not conflict with the phase rule. The fully mobile behaviour of such a component is expressed in the fact that depending on a slight change in the conditions, e.g., pressure, a significant precipitation or dissolution of such a component is possible. Such components may be designated as excessive fully mobile ones. An example of these in the course of low-temperature hydrothermal processes is furnished by silica and calcium, when quartz and calcite are removed from the wall-rocks and deposited in fissures in the form of veins. Thus fully mobile excess components, as distinguished from other fully mobile ones, may affect the number of co-existing minerals, namely, in that particular case when they are precipitated as independent minerals.

For many years the author has been studying the regularities of the mineral associations, particularly in metasomatic rocks. These empiric observations have led him to the idea of a fully mobile behaviour of a part of the components of any mineral system. The importance of this principle has been demonstrated in a number of the author's studies concerning metamorphic, metasomatic and, to some extent, magmatic rocks.

As an illustration of the application of the phase rule to natural semi-open systems we shall consider one of the diagrams obtained by the author in the course of a study of the paragenesis of minerals in the metasomatic rocks of the Archaean " Aldan-Slyudyanka " complex of East Siberia. In the zones of most intensive metasomatism a number of components behaves in a fully mobile way, namely, in the order of decreasing mobility: H_2O, CO_2, S, SO_3, Cl, K_2O, Na_2O, F, CaO, O_2, Fe. The constancy of the activity of these components is retained for metasomatic rocks of entire deposits, for the less mobile of the above-listed components a distinct dependence of activity upon the average composition of the wall-rocks being manifested: the richer the enclosing rocks in iron and calcium, the higher the activity (concentration) of these elements in the solutions producing metasomatism. Near marbles calcium behaves as an excessive fully mobile component; it is deposited as calcite in fissures and in a disseminated state in those silicate rocks the replacement of which is accompanied by decrease in volume. The activity of other mobile components for the belts of the most powerful manifestation of metasomatic processes shows a striking constancy, so that it is possible to speak of the definite composition of post-magmatic solutions, normal for this Archaean complex of rocks, as far as these more mobile components are concerned. The diagram in Fig. 1 shows the dependence of the mineralogical composition of metasomatic rocks, of the rocks of phlogopite deposits in

particular, on the ratio of the inert components Mg-Al-Si, with a composition of solutions normal for the Aldan-Slyudyanka complex, with an excess of calcium and with a low concentration of iron. It should be noted that the parageneses shown in this diagram are observed not only in the phlogopite deposits of Siberia but also in other Archaean phlogopite deposits, e.g., those of Canada and Madagascar.
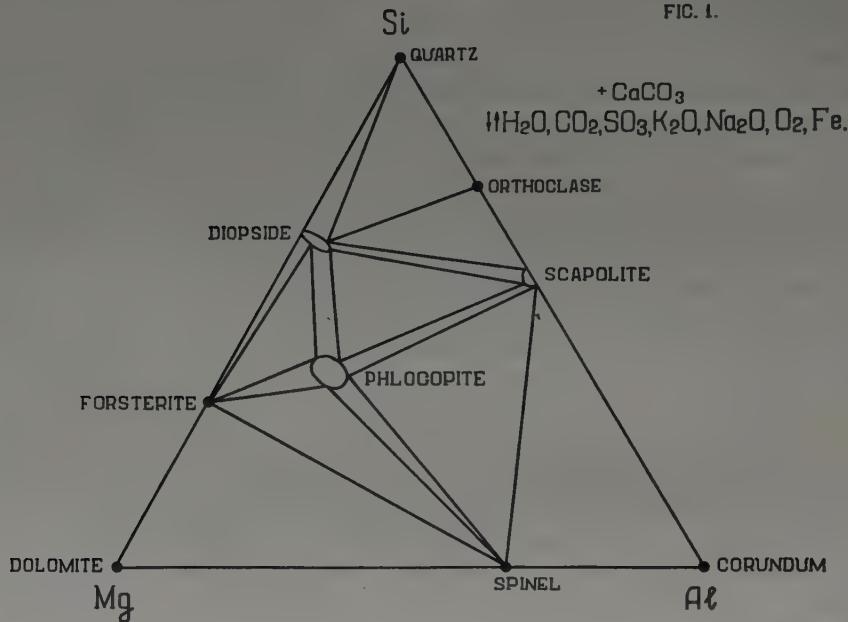

FIG. 1.—*Example of a composition-paragenesis diagram, equipotential with regard to a number of fully mobile components (written after the symbol of full mobility↓↑). Calcite in excess.*

The diagram shows that the ratio of the three inert components determines the content of the series of fully mobile ones. Thus, potassium may enter only into the composition of orthoclase or phlogopite, water only into the composition of phlogopite, the sulphate group, only into that of scapolite, i.e., these components enter into the composition of a rock only depending on the ratio of inert components in it. The ratio of inert components—aluminium, silicon, magnesium—depends on the content of these elements in the original rock, whereas the content of the fully mobile elements depends not on their initial content but on the ratio of the inert components, as well as on the temperature and the concentration of the solutions. A change in the concentration of the solution leads to a change of our diagram. Thus, with a higher concentration of iron in the solution, instead of the diopside + scapolite + phlogopite association hornblende appears. With a decreasing concentration of potassium, the association of spinel with diopside becomes possible, etc.

As shown in our diagram, the compositions of phlogopite, pyroxene and scapolite vary within a rather narrow range. Let it be supposed first that the composition of these minerals is constant, i.e., for each of these minerals it is shown by a point, just as for the other minerals in the diagram. Then any composition of the rock with an independent (occasional, arbitrary) ratio of the inert components will be represented by a point, lying inside one of the three-mineral triangles of the diagram, and the rock must be composed of three corresponding minerals. A coincidence of the point of an independent rock composition with the point of the composition of one of the minerals or with the two-mineral line of the diagram is excluded as an improbable one. Hence, any rock of this system within a given metasomatic facies must be composed of three minerals in accordance with the number of inert components in it ($p = n_i$).

Since some of the minerals are of a variable composition, as shown in the diagram, the point of

an arbitrary composition of a rock may fall not only into a three-mineral but also into a two-mineral or a one-mineral field. The number of inert components here is equal to the maximum number of co-existing minerals ($p \leqslant n_i$). A decrease in the number of the co-existing minerals accordingly increases the number of freedom degrees for the concentration of the inert components in the minerals ($p = n_i - f_{ci}$). However, these concentrations or activities, i.e., intensive parameters, are not independent but depend on occasional ratios of the amounts of inert components, that is on extensive factors. Thus, when minerals of a variable composition are present, in order to establish the number of inert components a study should be made of a set of rocks formed under the given conditions (in the given facies of metasomatism), the maximum number of minerals being determined.

If there is a diffusion of inert components, monomineral and bimineral rocks are formed even when the composition of minerals is a constant one. The theory of these phenomena has been discussed by the writer elsewhere. In particular the above-mentioned phlogopite deposits are formed at the expense of a diffusion interaction of dolomites and aluminium-silicate rocks in zones of an intense action of solutions, when the parageneses of the above diagram are realized. The reacting rocks are separated by zones of bimineral and monomineral rocks (diopside-scapolite, diopside phlogopite, diopside), three-mineral parageneses of our diagram being realized at the junctions of these zones.

In this way, when studying a series of rocks altered under conditions of one " metasomatic facies " we may establish the number of inert components, primarily from the maximum number of minerals. Next one should establish what components behave in an inert way. In doing this one starts from the fact that the content of inert components depends on the initial composition of the rock and not on the composition of the solutions, while the ratio of inert components definitely determines the content of all fully mobile components. As to the activity (concentration in the pore solution), for inert components it may vary from point to point, while for fully mobile components the activity is constant for the entire facies.

With any metamorphism or metasomatic action of solutions upon rocks a differential mobility of elements or oxides is displayed. In any given facies one part of the components displays inertness, while the others behave in a fully mobile manner. The more intensive the action of the solution, the greater the number of components passing into a mobile state, with a decrease of the number of inert components. By studying the set of such facies we may establish the series of decreasing relative mobility of elements and oxides. In any given process the less mobile components of this series behave inertly, whereas all the preceding more mobile components behave in a fully mobile manner.

Such is the fundamental principle of the method of establishing the relative mobility of components on the basis of an analysis of the paragenesis of minerals by means of the phase rule. This method has been developed by the author during several years, with a detailed study of the different geological complexes. The details of the method need not be discussed here, and only some of the inferences will be considered.

It has been found that the contrast of inert and mobile components is displayed not only in metamorphic but also in magmatic processes, when a number of components (water, potassium, sodium, etc.) behave in a fully mobile manner, as has been shown by the writer for granitoid rocks. This accounts for many peculiarities of magmatic rocks and processes.

The data obtained on the relative mobility of components will be considered next. Since mobility depends mainly on the solubility, it might be expected that the mobility series would sharply change for many reasons—depending on temperature, pressure, composition of solutions, composition of rocks. But it has been found that the relative mobility is determined essentially by two factors— the temperature stage and the depth, while the influence of the other factors has not been ascertained and seems to be insignificant. This points to a uniformity in the composition of ascending solutions. The mobility series obtained by the writer will be cited.

The " Aldan-Slyudyanka " Archaean gneissic complex of Eastern Siberia, enclosing phlogopite deposits, is one of the most abyssal complexes of the Earth. It is characterized by a development of hypersthene gneisses and a complete instability of wollastonite and grossularite, with regard to

depth being an analogue of the oldest Archaean gneisses of Canada, South Africa, Australia, etc. Here the writer has established for the high-temperature processes the following series of decreasing mobility: H_2O, CO_2, S, SO_3, Cl, K_2O, Na_2O, F, CaO, O_2, Fe, P_2O_5, BaO, MgO, SiO_2, Al_2O_3, TiO_2.

As an example of hypabyssal formations may be cited the eroded Devonian volcanic complex of the region of the well-known Tuhrya skarn copper deposits in the northern part of the Urals. The intrusive granitoids of this region, with which metamorphism and mineralization are associated, are closely related genetically to the invaded volcanic series, i.e., their intrusion occurred at a shallow depth. For the high- and medium-temperature metasomatic processes the author has established here the following mobility series:

H_2O, CO_2, S, K_2O, Na_2O, O_2, MgO, Fe, CaO, SiO_2, P_2O_5, Al_2O_3, TiO_2.
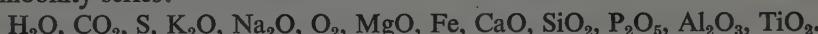
For the low-temperature processes the following series has been established:

H_2O, CO_2, S, K_2O, Na_2O, O_2, Cu, SiO_2, CaO, MgO, Fe, P_2O_5, Al_2O_3, TiO_2.
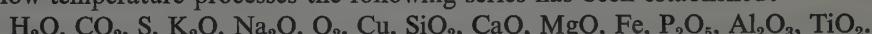
The studies carried out have shown that these series have a general significance for different formations of the corresponding depths.

At this point a survey of the behaviour of different oxides and elements during metamorphic, magmatic and post-magmatic processes will be made.

Water and carbon dioxide behave in a fully mobile way during any metamorphism, their activity being maintained on a constant level depending on temperature and for carbon dioxide sharply increasing with depth. Potassium and sodium are inert in the so-called "normal" metamorphism but fully mobile during any metasomatic process, as well as in processes of migmatization and granitization and during the crystallization of magma. The equalized concentration (activity) of potassium and sodium causes a uniformity of the mineralogical composition in migmatization haloes and in igneous rocks. Local increases of this concentration call forth the appearance of alkaline types of igneous rocks.

Oxygen has a limited mobility, particularly under more deep-seated conditions. This is accounted for by its insignificant concentration in magmas and in post-magmatic solutions, particularly at depth. Its inertness is displayed, for instance, in that both ferric and ferrous iron usually behave as independent components, with the exception of the more intensive metasomatic processes. It is of interest to note that while the mobility of oxygen is small and that of carbon quite insignificant (when it is present in the form of graphite), their compound carbon dioxide has a high mobility. This indicates a high concentration of carbon dioxide in natural solutions with a low concentration of its components, i.e., a weakness of its dissociation. Thus the study of mobility enables us to judge about the associated or dissociated state of substances in natural solutions. By this method we arrive at the conclusion that in solutions we have to do not with groups corresponding to separate minerals but with elements and oxides, probably in an ionized state.

Calcium in abyssal gneissic complexes has a considerably greater mobility than under shallow-depth conditions. This is obviously related to the above-mentioned increase in the carbon dioxide concentration with depth, which must increase the solubility of calcium. The mobility of calcium increases also with the falling temperature.

On the contrary, the mobility of iron sharply diminishes with a drop of temperature. At high temperatures, namely during the formation of andradite skarns and contact magnetite rocks, iron migrates on a huge scale. But during low-temperature processes iron is inert and is subject only to a restricted displacement in fracture zones, being removed from certain parts and forming accumulations in others. The mineralization with a formation of iron-bearing sulphides (pyrite, chalcopyrite, arsenopyrite) very often proceeds at the expense of the local inert iron, without any supply of iron from outside, e.g., in disseminated "porphyry" ores, or at the expense of iron supplied previously, during the high-temperature stage, as is the case in some skarn deposits. The large scale precipitation of magnetite from solutions in contact deposits seems to be partly due to a decrease in the solubility of iron with a drop of temperature.

Magnesium at shallow and medium depths has a significant mobility. Phenomena of magnesia

metasomatism in the sulphide deposits of Scandinavia, probably associated with medium depths, were established by P. Eskola and described by a number of workers. But the peculiar ore quartzites, cordierite-anthophyllite and other rocks, formed here, are rather unusual and the conditions of their formation are not quite clear. More widely known is an extensive migration of magnesium during the formation of skarn zones, when magnesium always behaves in a fully mobile manner. The extensive development of iron-magnesia clinopyroxenes is here independent of the presence or absence of magnesium in the adjacent limestones. But in the normal contact aureoles, too, a full mobility of magnesium is often displayed, resulting in a widespread but usually overlooked magnesia metasomatism, with the formation of hornfelses, very rich in biotite and amphibole. The uralitization of augite-plagioclase rocks too is generally accompanied by a supply of magnesium, the mobility of which is very common for post-magmatic processes. Unlike calcium, magnesium becomes less mobile with depth, so that their mutual arrangement in the mobility series sharply changes with depth. In the most abyssal Aldan-Slyudyanka gneissic complex, in spite of the intensity of the high-temperature metamorphism, magnesium does not anywhere behave in a fully mobile manner, while its local migration is observed only at contacts with dolomite, for instance during the formation of phlogopite deposits, as mentioned above. It is evidently the case of a low solubility of magnesium in deep-seated solutions, but the possible causes of this are not known.

Silica is highly mobile in low-temperature processes, when quartz veins and silicified rocks are readily formed. But in high-temperature processes it shows considerable inertness, and its migration is observed only at contacts of the rocks which are chemically not in equilibrium. Here a local migration of silica, mainly a diffusional one, takes place, as, e.g., when skarns are formed. High-temperature quartz bodies, associated with certain pegmatites, greisens, etc., are formed mainly at the expense of a removal of other components from acid rocks, and not at the expense of a supply of silica by solutions. It seems that the solubility of silica in the high-temperature solutions was low but that it increased with a drop of temperature. Hence it follows that the formation of common hydrothermal quartz veins could not have proceeded at the expense of a supply of silica from the cooling magmatic chamber, and could occur only at the expense of a migration of the silica of wall-rocks.

The low mobility of alumina is generally known. In the course of the most intensive metasomatic processes alumina not infrequently still retains inertness, when the other principal rock-forming elements have already passed into a fully mobile state. Under such conditions there are formed, for instance, at vein contacts monomineral wall-rocks composed, depending on the temperature and concentration of the fully mobile components, of one of the following aluminium silicates: albite, adularia, muscovite or sericite, chlorite, tourmaline, epidote, etc.

The most inert of all the common elements is titanium. It remains an inert component in all magmatic and metasomatic processes, with the exception of the processes of complete silicification, when it begins to be removed next to alumina. Due to such an inertness of titanium, its content may be used as an important criterion in determining the origin of a metasomatic rock (e.g., to distinguish skarns which have replaced limestones and an igneous rock).

The mobility of elements determines their behaviour in geochemical processes. The activity of inert components increases as the crystallization of magma proceeds, until they begin to segregate as separate minerals or entering into the composition of other minerals; the content of inert elements in an igneous rock therefore corresponds to their content in the magma. The activity of mobile elements does not increase to such a degree as the crystallization proceeds because of their diffusion and removal with the solutions. Hence it is possible for them not to take part in the composition of the igneous rock but to be deposited within a certain distance from the magmatic chamber. Titanium, zirconium, phosphorus are examples of inert components constituting the accessory minerals of igneous rocks; manganese, silver, gold, mercury are examples of extremely mobile elements of the magma.

A systematic analysis of the parageneses on the basis of the phase rule is an efficient method for studying the geochemical mobility of elements, which throws light also on problems of the composition and state of natural solutions and other peculiar features of geochemical processes.

ПРАВИЛО ФАЗ И ГЕОХИМИЧЕСКАЯ ПОДВИЖНОСТЬ ЭЛЕМЕНТОВ

Д. С. КОРЖИНСКИЙ

Одной из основных задач геохимии, по учению русских академиков В. И. Вернадского и А. Е. Ферсмана, является изучение геохимической миграции элементов. Поэтому геохимическая подвижности т.е. способность элементов и окислов мигрировать (перемещаться) при природных процессах образования и изменения горных пород и руд, является важным геохимическим их свойством. Подвижность для разных компонентов весьма различна и связана главным образом с растворимостью данного компонента в природных жидких растворах, присутствие которых необходимо для образования минералов, по крайней мере силикатовых. Но, кроме того, имеет значение способность компонента диффундировать и способность просачиваться с раствором через поры горных попрод (фильтрационный эффект).

При изучении геохимической подвижности элементов особенно большое значение имеет систематический анализ закономерностей ассоциации минералов на основе правила фаз.

Правило фаз Гиббса, как известно, дает связь между числом компонентов n, числом фаз p и числом степеней свобод в равновесной системе:

$$f + p = n + 2$$

К минеральным ассоциациям горных пород правило фаз впервые было применено В. Гольдшмидтом (1911) в упрощенном виде „минералогического правила фаз“ ($p \leqq n$). С тех пор правило фаз прочно вошло в петрографию и использовалось многими авторами для установления равновесности или неравновесности минеральных ассоциаций в горных породах и как основа для графического анализа и изображения равновесных ассоциаций горных пород.

Но, кроме того, правило фаз, как оказывается, может быть использовано установления относительной подвижности элементов, к чему мы и обратимся.

Физико-химические параметры или величины, характеризующие состояние системы, могут быть разделены на интенсивные и экстенсивные. Первые не зависят от масс отдельных фаз в системе или соотношения этих масс, а вторые зависят. К факторам интенсивности относятся температура, давление, концентрации компонентов в фазах. К факторам экстенсивности относятся содержание тепла в системе, ее объем, содержания компонентов в системе.

Правило фаз Гиббса принимает во внимание только параметры интенсивности. Число независимых параметров интенсивности, т.е. число степеней свободы f, согласно этому правилу, равно $(n + 2 - p)$. Каково же общее число независимых интенсивных и экстенсивных параметров в системе $(f_i + f_e)$? Если мы зададим систему при помощи всех ее независимых интенсивных параметров $f_i = n + 2 - p$ и добавим сюда еще массы каждой из фаз, т.е. p независимых экстенсивных параметров, то, очевидно, система будет вполне определена, при общем число независимых параметров $f_i + f_e = (n + 2 - p) + p = n + 2$. Итак, общее число независимых параметров системы, интенсивных и экстенсивных, не зависит от числа фаз в ней, а только от числа компонентов, именно это число на два больше числа компонентов

В отношении абстрактной физико-химической системы безразлично, какие из параметров считать независимыми, а какие зависимыми: безусловным является только общее число независимых параметров. Мы можем принять независимыми одни экстенсивные факторы, задав систему массами каждого из n компонентов, общим объемом и теплосодержанием системы,

т.е. = 2 экстенсивными параметрами. Тогда все остальные экстенсивные и интенсивные параметры будут функциями всятых независимых параметров. Но мы можем часть экстенсивных факторов заменить соответствующими интенсивными, т.е. вместо объема системы задать давление, вместо теплосодержания системы—температуру, вместо содержания компонента в системе—концентрацию его в одной из фаз или же активность или химический потенциал его в системе. Однако число независимых факторов интенсивности f_i не может превышать числа n + 2 — p, т.е.

$$f_i + f_e = n + 2$$
$$f_i \leqq n + 2 - p$$
$$p \leqq f_e \leqq n + 2$$

Но в конкретных системах состояние задается вполне определенными факторами и потому разделение параметров на независимые и зависимые теряет свою произвольность, становится однозначным. Некоторые параметры даются внешними условиями процесса или исходным состоянием системы; такие „извне-заданные" параметры, не зависящие от физико-химических свойств данной системы, всегда являются, конечно, независимыми факторами равновесия. Величина других, зависимых, параметров останавливается на уровне, зависящем как от физико-химических свойств данной системы, так и от извне-заданных факторов. Для понимания природного процесса, приведшего к данному состоянию разновесия, очень существенно установление экстенсивного или интенсивного характера внешних факторов процесса и в этом отношении может помочь применение правила фаз.

В процессах образования минералов и горных пород в земной коре, в силу возможности диффузия тепла и изменения объема, внешними факторами являются не экстенсивные параметры—теплосодержание и объем, а, как предположил В. Гольдшмидт, интенсивные параметры—температура и давление. Тем самым, для каждой равновесной минеральной ассоциации число независимых интенсивных параметров понижается на два, откуда и получае „минералогическое правило фаз" Гольдшмидта (p ≤ n). Практика применения правила фаз к горным породам вполне оправдала допущение В. Гольдшмидта о температуре и давлении как независимых факторах минералообразования.

Что касается состава то в закрытой системе он, очевидно, определяется одними экстенсивными факторами—содержанием компонентов в исходном состоянии. Но возможен случай, когда только для части компонентов содержание в конечном равновесном состоянии системы будет зависет от исходного содержания, тогда как для остальных содержание будет зависеть от заданной концентрации этих комнопентов в притекающем растворе или вообще определяться активностью этих компонентов во внешней среде. Следовательно, подобно тому как тепловой режим системы может быть обусловленными в одних случаях постоянным содержанием тепла (системы с тепловой изоляцией), а в других случаях температурой окружающей среды, так и содержание данного компонента в одних случаях может быть обусловлено первичным содержанием, а в других случаях активностью его в окружающей среде. Дело идет, следовательно, в полуоткрытых системах, замкнутых для одних и открытых для других компонентов.

В лаборатории мы встречаемся с полуоткрытой системой, например, при прокаливании нелетучих веществ в открытом тигле. Содержание этих веществ в тигле не изменяется, тогда как содержание кислорода и азота для равновесных состояний будет зависеть не от первичного их содержания в тигле, а от давления их в атмосфере и от характера и содержания нелетучих веществ в тигле. Другим примером является мембранное (осмотическое) равновесие. При природных процессах образования и изменения пород полуоткрытые системы осуществляются благодаря тому, что некоторые компоненты плохо растворимы в воздействующих на породы водных растворах, а потому не перемещаются, тогда как другие хорошо растворимы, хорошо диффундируют через раствор или хорошо просачиваются вместе

с раствором через боковые породы, а потому их активность в горной породе должна соответствовать таковой в притекающем растворе.

Компоненты, которые при процессах данного типа не изменяют своего содержания, назовем ,,вполне инертными'' при данных процессах. Компоненты, содержание которых не зависит от первичного содержания, а определяется активностью во внешней среде (например, концентрацией в притекающих растворах), назовем ,,вполне подвижными'' при данном типе процессов. Это два крайних идеальных случая. Но последующие выводы применимы и к таким более естественным случаям, когда инертные компоненты могут несколько менять свое содержание, однако не в такой степени, чтобы отступление от идеальной инертности привело к изменению типа или число фаз в рассматриваемой системе.

Прилагая правило фаз к минеральным ассоциациям, мы вправе в качестве фаз рассматривать только минералы, хотя несомненно, что образование и изменение горных пород, по крайней мере силикатовых, происходило при участии тех или иных растворов, затем удалившихся.

Отбросив две степени свободы, связанные с извне-заданными температурой и давлением, мы получим правило фаз в сдедующем виде:

$$p = n - f_c$$

где f_c—обозначает число независимых (свободных) концентрации компонентов. Число минералов в равновесной ассоциации равно, таким образом, числу компонентов минус число свободных концентраций. Однако, в конкретных случаях только часть f_{cm} из этих свободных концентраций меняется действительно независимо, представляя собой извне заданные концентрации вполне подвижных компонентов. Другая часть f_{ci} это число степеней свобод тех возможных вариаций состава минералов, которые зависят от вариаций содержания инертных компонентов в системе и потому не являются независимыми. Возможны системы минералов постоянного состава, не допускающего вариаций в отношении рассматриваемых инертных компонентов. Для таких систем число свободных концентраций f_c равно числу вполне подвижных компонентов n_m, тогда как **число минералов постоянного состава в равновесной ассоциации равно числу инертных компонентов** n_i:

$$n = n_i + n_m; \quad f_c = n_m; \quad p = n - f_c = n_i; \quad n_m = n - p.$$

Число подвижных компонентов равно, очевидно, разности между общим числом компонентов и числом минералов. Такми образом, в предельном случае полного отсутствия твердых растворов, определив число минералов в равновесной ассоциации и число присутствующих в них элементов, мы могли бы установить, какое число из этих элементов вело себя при образования породы вполне подвижным образом.

В общем случае присутствия минералов переменного состава имеем:

$$f_c \geqq n_m; \quad p \leqq n_i; \quad n_m \leqq n - p; \quad p = n_i - f_{ci}$$

т.е. **максимальное число минепалов в равновесной ассоциации равно числу инертных компонентов и не зависит от числа вполне подвижных компонентов.**

Как видно из приведенных формул, при применении правила фаз можно пренебречь наличием в системе вполне подвижных компонентов, соответственно уменьшив одновременно и число компонентов и число свободных концентраций. Точно так же и при графическом анализе зависимости минералогического состава от химического достаточно принять во внимание только инертные компоненты, если изучается серия пород или руд, образовавшихся при неизменных условиях температуры, давления и концентрации притекающих растворов. Действительно, независимые вариации состава возможны только в отношении инертных компонентов, и минералогический состав, при постоянстве указанных внешних условий, является функцией соотношения инертных компонентов.

Рассссмотренная противоположность в поведении инертных и вполне инертных компонентов должна проявляться не только в идеальных полуоткрытых системах, вполне замкнутых

в отношении инертных компонентов. Эта противоположность должна иметь место и в более естественных системах, в которых все компоненты обладают подвижностью, но в различной степени. В силу дифференциальной подвижности компонентов, полное выравнивание активности в породе с активностью в притекающих растворах успевает произойти только для наиболее подвижных компонентов. Для менее подвижных компонентов хотя и могут происходить перемещения, но для них еще сохраняются вариации исходного состава, не связанные с различиями в составе притекающих растворов. Вообще говоря, если идеальная замкнутость системы для инертных компонентов нарушается и содержание их начинает изменяться, то это приводит сначала к изменению относительных количеств фаз и к изменению их состава, без изменения числа фаз или их типа, т.е. без нарушения инертности поведения таких компонентов в рассмотренном выше смысле

Особый случай представляет вполне подвижный компонент, концентрация которого поддерживается внешними условиями на уровне насыщения, при котором возможно выпадение этого компонента в числом виде или в соединении с другими вполне подвижными компонентами. Такая концентрация, очевидио, не является свободной, не связанной, и поэтому возможное появление дополнительной фазы не противоречит правилу фаз. Вполне подвижное поведение такого компонента сказывается в том, что в зависимости от небольшого изменения условий, например, давления, возможно значительное выделение или растворение такого компонента. Такие компоненты могут быть образоначены как ,,избыточные вполне подвижные.`` Примером их при низкотемпературных гидротермальных процессах могут служить кремнезем и кальций, когда кварц и кальцит выносятся из боковых пород и отлагаются в трещинах в виде жил. Итак, вполне подвижные избыточные компоненты, в отличие от других вполне подвижных, могут влиять на число сосуществующих минералов—именно в том случае, когда они выпадают в виде самостоятельных минералов.

Автор в течение многих лет занимался исследованием закономерностей ассоциаций минералов, в особенности в метасоматических породах. Именно эти эмпирические наблюдения привели его к представлению о вполне подвижном поведении части компонентов каждой минеральной системы. Плодотворность этого принципа показана в ряде исследований автора или метаморфических, метасоматических и отчасти магматических пород.

В качестве примера применения правила фаз к природным полуоткрытым системам рассмотрим одну из диаграмм, полученных автором при изучении парагенезисов минералов в метасоматических породах архейсклшл ,,Алдано-Слюдянского`` комплекса Восточной Сибири. В зонах наиболее интенсивного метасоматоза здесь целый ряд компонентов ведет себя вполне подвижным образом, а именно, в порядке понижающейся подвижности: H_2O, CO_2, S, SO_3, Cl, K_2O, Na_2O, F, CaO, O_2, Fe. Постоянство активности этих компонентов сохраняется для метасоматических пород целых месторождений, причем для менее подвижных из перечисленных компонентов обнаруживается зависимость активности от среднего состава боковых пород—чем богаче вмещающие породы железом и кальцием, тем выше была активность (концентрация) этих элементов в растворах, производивших метасоматоз. Вблизи мраморов кальций ведет себя как избыточный вполне подвижный компонент; он отлагается в виде кальцита в трещинах и рассеянно в тех силикатовых породах, замещение которых сопровождается уменьшением объема. Активность других подвижных компонентов, для поясов наиболее мощно проявившихся метасоматических процессов, обнаруживает удивительное постоянство, так что можно говорить о некотором нормальном для данного комплекса пород составе постмагматических растворов в отношении этих более подвижных компонентов. Диаграмма рис. 1 дает зависимость минералогического состава метасоматических пород, в частности пород месторождений флогопита, от соотношения в них инертных компонентов Mg—Al—Si при нормальном для Алдано-Слюдянского комплекса составе растворов, при избытке кальция и при низкой концентрации железа. Надо сказать, что парагенезисы этой диаграммы осуществляются не только в флогопитовых месторож-

дениях Сибири, но и в других архейских флогопитовых месторождениях, например, Канады и Мадагаскара.

На этой диаграмме мы видим, что соотношение трех инертных компонентов определяет содержание ряда вполне подвижных. Так, калий может войти в состав ортоклаза или флогопита; вода—только в состав флогопита; сульфатная группа—только в состав скаполита,— т.е. эти компоненты входят в состав породы только в зависимости от соотношения в ней инертных компонентов. Соотношение инертных элементов—алюминия, кремния, магния— зависит от содержания этих элементов в исходной породе, тогда как содержание вполне подвижных элементов зависит не от первичного их содержания, а от содержания инертных, а также от температуры и от концентрации растворов. Изменение концентрации раствора ведет к видоизменению нашей диаграммы. Так, с повышением в растворе концентрации железа вместо ассоциации диопсид + скаполит + флогопит появляется роговая обманка. При понижении концентрации калия становится возможной ассоциация шпинели с диопсидом и т.д.

Как показано на нашей диаграмме, составы флогопита, пироксена и скаполита меняются в нешироких пределах. Предположим, сначала, что состав этих минералов постоянен, т.е. изображается для каждого из этих минералов точкой, как это имеет место для других минералов диаграммы. Тогда любой состав породы с независимо (случайно, произвольно) заданным соотношением инертных компонентов изобразится точкой, лежащей внутри одного из трех-минеральных трегуольников диаграммы, и порода должна быть сложена тремя соответствую-щими минералами. Совпадение независимо заданной точки состава породы с точкой состава одного из минералов или с двуминеральной линией диаграммы исключается как невероятное попадание. Следовательно, любая порода этой системы в пределах данной метасоматической фации должна быть сложена тремя минералами соответственно числу инертных компонентов в ней (p = n).

Поскольку некоторые минералы имеют переменный состав, как показано на диаграмме, точка произвольно заданного состава породы может попасть не только в трехминеральное, но также и в двуминеральное или одноминеральное поле. Число инертных компонентов здесь равно максимальному числу минералов (p $\leq$ n). С уменьшением числа сосуществующих минералов соответственно возрастает число степеней свобод в отношении концентрации инертных компонентов в минералах (p = n_i — f_{ci}). Однако, эти концентрации или актив-ности, т.е. интенсивные параметры, не являются независимыми, извне заданными, а зависят от случайных соотношений содержаний инертных компонентов, т.е. зависят от экстенсивных факторов. Итак, при наличии минералов переменного состава, для установления числа инертных компонентов должна изучаться серия пород, образовавшихся в данных условиях (в данной фации метасоматоза), с определением максимального числа минералов, а иногда и характера вариаций состава переменных минералов.

При наличии диффузии инертных компонентов возникают мономинеральные и биминеральные породы даже при постоянном составе минералов. Теория этих явления рассмотрена мною в другом место. В частности, упомянутые флогопитовые месторождения образуются за счет диффузионного взаимодействия доломитов с алюмосиликатовыми породами в зонах интенсивного воздействия растворов, когда осуществляются парагенезисы рассмотренной диаграммы. Реагирующие породы отделяются при этом зонами биминеральных и моно-минеральных пород (диопсид-скаполитовая, диопсид-флогопитовая, диопсидовая), причем на стыках этих зон осуществляются трехминеральные парагенезисы нашей диаграммы.

Итак, изучая серию пород, измененных в условиях одной „метасоматической фации,‘‘ мы можем установить число инертных компонентов, преимущественно по максимальному числу минералов. Далее надо установить, какие именно компоненты ведут себя инертно. Здесь мы опираемся на то, что содержание инертных компонентов зависит от исходного состава породы, а не от состава растворов, а соотношение инертных компонентов однозначно

определяет содержание вполне подвижных компонентов.   Что касается активности (концен-трации в поровом растворе), то для инертных компонентов она может меняться от точки к точке, тогда как для вполне подвижных компонентов активность постоянна для всей фации.

При всяком метаморфизме или метасоматическом воздействии растворов на горные породы проявляется дифференциальная подвижность элементов или окислов.   В каждой данной фации часть компонентов проявляет инертность, в то время как другие ведут себя вполне подвижно.   Чем интенсивнее воздействие раствора, тем большее количество компо-нентов переходит в вполне подвижное состояние, с уменьшением числа инертных компонентов. Изучая совокупность таких фаций, мы можем установить ряд убывающей относительной подвижности элементов и окислов.   При каждом данном процессе менее подвижные компо-ненты этого ряда ведут себя инертно, а все предшествующие им более подвижные компоненты ведут себя вполне подвижно.

Таков основной принцип метода установления относительной подвижности компонентов на основе анализа парагенезисов минералов при помощи правила фаз.   Метод этот развивался автором в течение ряда лет при детальном исследовании различных геологических комплексов. Здесь нет надобности входить в детали метода и мы ограничимся некоторыми полученными выводами.

Оказалось, что противоположность инертных и подвижных компонентов проявляется не только при метаморфических, но и при магматических процессах, при которых ряд компо-нентов (вода, калий, натрий и др.) ведут себя вполне подвижно, как это было показано автором для гранитоидных пород.   Этим объясняются многие особенности магматических пород и процессов.

Обратимся теперь к полученным данным по относительной подвижности компонентов. Поскольку подвижность зависит главным образом от растворимости, то можно было бы ожидать, что ряд подвижности будет резко меняться от многих причин—от температуры, состава растворов, составе пород   Но оказалось, что относительная подвижность в основном определяется двумя факторами—температурной стадией и глубинностью, тогда как влияние других факторов не выяснено и, видимо, назначительно.   Это указывает на однообразие состава глубинных растворов.   Приведем полученные нами ряды подвижности.

„Алдано-Слюдянский'' архейский гнейсовый комплекс Восточной Сибири, включающий месторождения флогопита, принадлежит к наиболее глубинным образованиям земли.   Он характеризуется развитием гиперстеновых гнейсов и полной неустойчивостью волластонита и гроссуляра, будучи в отношении глубинности аналогом древнейшим архейским гнейсам Канады, Южной Африки, Австралии и проч.   Здесь для высокотемпературных процессов автором установлен ряд убывающей подвижности.

H_2O, CO_2, S, SO_3, Cl, K_2O, Na_2O, F, CaO, O_2, Fe, P_2O_5, BaO, MgO, SiO_2 Al_2O_3, TiO_2
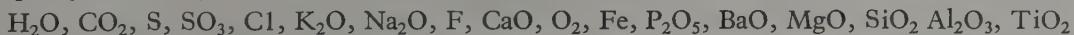
Как пример гипабиссальных образований, может быть взят размытый девонский вулкани-ческий комплекс района известных Турьинских скарновых медных месторождений в северной части Урала.   Интрузивные гранитоиды этого районо, с которыми связаны метаморфизм и оруденение, генетически тесно связаны с прорываемой ими в улканической толщей, т.е. внедрялись на малой глубине.   Для высокотемпературных и среднетемпературных метасома-тических процессов здесь установлен автором следующий ряд подвижности:

H_2O, CO_2, S, K_2O, Na_2O, O_2, MgO, Fe, CaO, SiO_2, P_2O_5, Al_2O_3, TiO_2
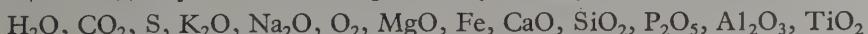
Здесь же для низкотемпературных процессов установлен следующий ряд:

H_2O, CO_2, S, K_2O, Na_2O, O_2, Cu, SiO_2, CaO, MgO, Fe, P_2O_5, Al_2O_3, TiO_2
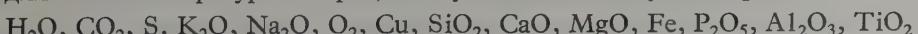
Исследования показывают, что эти ряды имеют общее значение для различных формаций соответствующих глубин.

Сделаем теперь обзор поведения различных окислов и элементов при метаморфических магматических и постмагматических процессах.

Вода и углекислота ведут себя вполне подвижно при всяком метаморфизме. Активность их при этом поддерживается на постоянном уровне, зависимом от температуры и для углекислоты резко возрастающем с глубиной. Калий и натрий инертны при так и зываемом „нормальном" метаморфизме, но вполне подвижны при всяком метасоматическом процессе, а также при явлениях мигматизации и гранитизации и при кристаллизации магм. Уравнительная концентрация калия и натрия обусловливает однообразие минералогического состава в ореолах мигматизации и в изверженных породах. Местные повышения этой концентрации обусловливают появление щелочных типов изверженных пород.

Кислород обладает ограниченной подвижностью, особенно в более глубинных условиях. Это объясняется ничтожной его концентрацией в магмах и постмагматических растворах, особенно на глубине. Инертность его проявляется, например, в том, что окисное и закисное железо ведут себя обычно как самостоятельные компоненты, за исключением более интенсивных метасоматических процессов. Интересно, что при малой подвижности кислорода и совсем ничтожной—углерода (когда они присутствует в виде графита), их соединение—углекислота—обладает высокой подвижностью. Это указывает на высокую концентрацию углекислоты в природных растворах при низкой концентрации ее компонентов, т.е. слабость ее диссоциации. Таким образом, изучение подвижности дает нам возможность судить об ассоциированном и диссоциированном состоянии веществ в природных растворах. Таким методом мы приходим к заключению, что в растворах мы не имеем групп соответствующих отдельным минералам, но элементы и окислы, вероятно, в ионизированном состоянии.

Кальций в глубинных гнейсовых комплексах обладает значительно большей подвижностью, чем в условиях малых глубин. Это, очевидно, связано с упомянутым возрастанием с глубиной концентрации углекислоты, что должно увеличивать растворимость кальция. Подвижность кальция возрастает также и с понижением температуры.

Наоборот, подвижность железа резко понижается с понижением температуры. При высоких температурах, именно при образовании андрадитовых скарнов и контактовых магнетитовых руд, железо перемещается в громадных масштабах. Но при низкотемпературных процессах железо инертно и обнаруживает только ограниченное перемещение в трещинных зонах, с выносом его в одних участках и образованием скоплений в других. Оруденение с образованием железосодержащих сульфидов (пирит, халькопирит, арсенопирит) очень часто происходит за счет местного инертного железа, без его привноса, например, во вкрапленных „порфировых" рудах, или за счет железа, привнесенного ранее в высокотемпературную стадию, как это имеет место в некоторых скарновых месторождениях.

Массовое осаждение растворами магнетита в контактовых месторождениях отчасти, повидимому, обусловлено понижением растворимости железа с понижением температуры.

Магний на небольших и средних глубинах обладает существенной подвижностью. Явления магнезиального метасоматоза в сульфидных месторождениях Скандинавии, относящихся, повидимому к средним глубинам, были, как известно, установлены П. Эскола и описаны рядом авторов. Но образующиеся здесь своеобразные рудные кварциты, кордиеритантофиллитовые и прочие породы довольно необычны и условия их образования не совсем ясны. Более известен широкий вынос магния при образовании скарновых зон, при образовании которых магний всегда ведет себя вполне подвижно. Широкое развитие железомагнезиальных клинопироксенов имеет место здесь независимо от наличия или отсутствия магния в прилежащих известняках. Но и в нормальных контактовых ореолах очень часто обнаруживается полная подвижность магмы, приведящая у широко распространенному, но обычно не замечаемому магнезиальному метасоматозу, с образованием роговиков, весьма богатых биотитом и амфиболом. Уралитизация авгит-плагиоклазовых пород тоже обычно сопровождается привносом магния, подвижность которого весьма обычна для постмагматических процессов. С глубиной магний, в противоположность кальцию, становится менее подвижным, так что взаимное их расположение в ряду подвижности с глубиной резко меняется.

В наиболее глубинном Алдано-Слюдянском гнейсовом комплексе, несмотря на интенсивность высокотемпературного метаморфизма, магний нигде не ведет себя вполне подвижно, а местная миграция его наблюдается только в контактах с доломитами, например, при образовании флогопитовых месторождений, как мы отмечали выше. Дело идет, очевидно, о малой растворимости магния в глубинных растворах, но возможные причины этого неясны.

Кремнезем весьма подвижен при низкотемпературных процессах, когда легко образуются кварцевые жилы и окварцованные породы. Но при высокотемпературных процессах он, оказывается, обнаруживает значительную инертность и его перемещение наблюдаются только в контактах химически неравновесных пород, где имеет место местная его миграция, преимущественно диффузионная, например, при образовании скарнов. Высокотемпературные кварцевые тела, связанные с некоторыми пегматитами, грейзенами и проч., образуются в основном за счет выноса других компонентов из кислых пород, а не за счет привноса растворами кремнезема. Очевидно, что растворимость кремнезема в высокотемпературных растворах была низка, но возрастала при понижении температуры. Отсюда следует, что образование обычных кварцевых жил не могло происходит за счет привноса кремнезема из остывающего магматического очага, но только за счет перемещения кремнезема боковых пород.

Малая подвижность глинозема общеизвестна. При наиболее интенсивных метасоматических процессах глинозем нередко сохраняет еще инертность, когда остальнае главные породообразующие элементы уже перешли в вполне подвижное состояние. В таких условиях возникают, например, мономинеральные околожильные породы, сложенные в зависимости от температуры и концентрации вполне подвижных компонентов одним из следующих алюмосиликатов: альбит, мусковит, или серицит, хлорит, турмалин, эпидот и проч.

Наиболее инертен из всех обычных элементов титан. Он остается инертным компонентом при всех магматических и метасоматических процессах, за исключением процессов полного окварцевания, когда он начинает выноситься вслед за глиноземом. В силу такой инертности титана, его содержание может быть использовано как важный критерий при определении происхождения метасоматической породы (например, для различения скарнов, заместивших известняк или изверженную породу).

Подвижность элементов определяет их поведение при геохимических процессах. Активность инертных компонентов по мере кристаллизации магмы возрастает, пока они не начнут выделяться в виде отдельных минералов или в составе других минералов; содержание инертных элементов в изверженной породе соответствует поэтому их содержанию в магме. Активность подвижных элементов по мере кристаллизации не повышается в такой степени, в силу их диффузии и ухода с растворами. Поэтому они могут не войти в состав изверженной породы, а отложиться в удалении от магматического очага. Титан, цирконий, фосфор служат примерами инертных компонентов, слагающих аксцессорные минералы изверженных пород: марганец, серебро, золото, ртуть являются примерами крайне подвижных элементов магмы.

Систематический анализ парагенезисов на основе правила фаз является плодотворным методом изучения геохимической подвижности элементов, бросающим свет также на вопросы состава и состояния природных растворов и другие особенности геохимических процессов.

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COMPOSITION OF THE MINERALS IN THE ROCKS OF THE SOUTHERN CALIFORNIA BATHOLITH

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ABSTRACT

The great complex batholith of Southern California contains rocks that range from calcic gabbro to granite and nearly all the analyses of the rocks fall near smooth variation curves, indicating a close consanguinity. The minerals of the rocks were studied with especial reference to the relation between the composition of the minerals and that of the enclosing rocks. The ratio $\dfrac{FeO}{FeO + MgO}$ is about the same for any rock as for all the mafic minerals in that rock. For hornblende the ratio is commonly a little low. The ratio is 0·36 in the calcic gabbros, and increases along a smooth curve to 0·85 in the granites. The anorthite content of the plagioclase changes regularly with the composition of the rock.

The minerals of the coarse-grained rocks of California are compared with the phenocrysts of the volcanic rocks of the San Juan region of Colorado. In the volcanic rocks the ratio $\dfrac{FeO}{FeO + MgO}$ does not change systematically with the composition of the rock. The biotites and hornblendes of the volcanic rocks contain less K_2O and more Fe_2O_3, and the orthoclase more Na_2O than do those minerals in the granular rocks.

The Batholith

THE batholith of Southern California extends from near Riverside, California to the southern part of Lower California. It is about 70 miles wide in California and is about 1,200 miles long.

A part of this great batholith has been mapped and studied by Larsen and a report is in the press (Larsen, 1948). The batholith is made up of many separate bodies which range from gabbro to quartz diorite, granodiorite, and granite. The rocks form a rather simple magma series and nearly all the rock analyses fall near smooth variation curves. The series is high in SiO_2 and low in K_2O.

The purpose of this paper is to report the chemical compositions of the minerals of the batholith and point out the relation between the compositions of the minerals and of the rocks enclosing them.

AUGITE AND OLIVINE

Augite is an abundant mineral in the gabbros and remnants of it are rare in the tonalites. For augite in gabbro Miller (1937, p. 1416) gives the range of optical properties as: $\alpha = 1\cdot686 - 1\cdot694$, $\beta = 1\cdot691 - 1\cdot700$, $\gamma = 1\cdot710 - 1\cdot719$, $+ 2V = 55° - 62°$, $r > v$ perceptible, $Z \wedge c = 39° - 44°$.

Olivine is found only in the gabbros with calcic feldspar. Miller (1937, p. 1416) gives its optical properties as $\alpha = 1\cdot682 - 1\cdot693$, $\beta = 1\cdot704 - 1\cdot716$, $\gamma = 1\cdot720 - 1\cdot735$, $- 2V = 80° - 86°$, $r > v$ distinct. These data indicate 25 to 31 per cent of Fe_2SiO_4.

HYPERSTHENE

Hypersthene is present in many of the gabbros and norites and in a few of the granites. It was not found in the tonalites and granodiorites.

An analysis and other data for a hypersthene from a norite are given in Table 1, column 1. This hypersthene is much like hypersthene in most gabbros and basaltic rocks and is somewhat similar to the hypersthene found in phenocrysts in a dark quartz latite, near basalt, from the San Juan

Mountains of Colorado, which is represented in column A (Larsen and others, 1936, pp. 695-6).

Rare hypersthene, very high in iron, was found in some of the granites. The coarse grained granite from Rubideaux Mountain, Riverside, California, contains less than one per cent of hypersthene and an analysis and other data on that mineral are given in Table 1, column 2.

TABLE 1. *Analyses of Hypersthene, by F. A. Gonyer*

	1	A	2
SiO_2	52·01	51·58	44·52
TiO_2	0·35	0·45	1·39
Al_2O_3	1·92	1·70	4·76
Fe_2O_3	1·99	3·15	1·26
FeO	19·78	18·11	38·66
MnO	0·22	0·39	0·28
MgO	20·92	22·01	6·59
CaO	2·78	1·82	1·40
Na_2O	0·11	...	0·39
K_2O	...	...	0·19
H_2O+	0·15	0·40	0·41
Sum	100·23	99·61	99·85
Formulæ:			
Mg	1·46	1·23	0·41
Fe″	0·61	0·56	1·33
Mn	0·01	0·01	0·01
Ca	0·11	0·07	0·06
Na	0·01	...	0·05
Fe‴	0·06	0·09	0·04
Al	0·04	0·02	0·12
Al	0·05	0·06	0·12
Ti	0·02	0·01	0·04
Si	1·93	1·93	1·84
O	6·0	6·0	6·0
α	1·701	1·702	1·752
β	1·708	1·707	1·759
γ	1·711	1·712	1·765
2V	(−)58	...	(−)78
α	Pale tanish green	Pink	Pale pink
β	Pale tan green	Yellow	Pale pinkish green
γ	Pale green	Green	Pale green

1. Hypersthene from norite (SLR M334) from three miles east of Vista. Chief minerals are plagioclase (An 64), augite, and hypersthene.

A. Hypersthene from dark quartz latite, near basalt (SV9) from the Sammitville quadrangle, Colorado (Larsen and others, 1936, pp. 695–6). The rock contains phenocrysts of plagioclase (An 47), augite, and hypersthene in a quartz latite groundmass.

2. Hypersthene from coarse granite (E138–167) from Rubideaux Mountain, near Riverside, California. Rock contains quartz, microperthite, plagioclase (An 20), a little biotite, and less than 1 per cent of hypersthene.

Miller (1937, p. 1416) has shown that in the gabbros the indices of refraction of the hypersthene increase with the albite content of the associated plagioclase. The index of refraction of the hypersthenes are plotted against the An content of the plagioclase in Figure 1.

BIOTITES

Biotite is present in nearly all the rocks that contain quartz, from the silicious norites to the granites. In the norites it is a late mineral to crystallize, in the granites it is in part an early mineral. Eight biotites from rocks ranging from norite to granite have been analysed by F. A. Gonyer and the analyses and other data are given in Table 2.

In Figure 2 the compositions of the biotites are plotted against the position of the enclosing rock on a variation diagram. (Larsen, 1938). The FeO in the biotites from the gabbro-diorites is less than 16 per cent, it increases slowly to about 20 per cent in the biotite from the granodiorites and rapidly
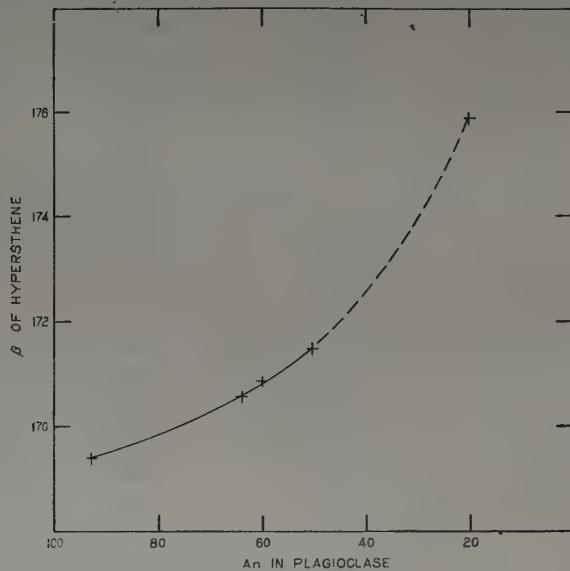

FIG. 1.—*The index of refraction of hypersthene plotted against the anorthite content of the associated plagioclase.*

to over 26 per cent in those from the granites. MgO changes inversely as the iron. Al_2O_3 is near 17 per cent in the biotites from the gabbros and tonalites and only about 14 in those from the granodiorites and granites. The other oxides show no systematic variation on the curves.

AMPHIBOLES

Amphibole is the most widespread femic mineral in the batholith. It is in variable amount in the gabbros, is the chief dark mineral in most of the tonalites, and is subordinate to biotite in the granites. In some of the gabbros it is the only dark mineral, in others it is absent. In all the gabbros it is a late magmatic or deteric mineral and commonly replaces pyroxene. Much of it is in large uniform grains but some is uralitic. The amphiboles in the gabbros are variable in colour and in other respects. In Table 3 eleven analyses of amphiboles are given, five from gabbros, three from tonalites, two from a granodiorite, and one from a granite.

TABLE 2. *Analyses and other data on Biotites*

|	1	2	3	4	5	6	7	8
		Green Valley	*Lakeview*	*Bonsall*	*Bonsall grano-diorite*	*Woodson grano-diorite*	*Rubideaux granite coarse*	*Rubideaux granite fine*
	Norite El 230	*tonalite* SLR 138	*tonalite* El 38–134	*tonalite* SLR 1016	SLR 2242	Ra 135	El 38–167	El 38–265
SiO_2	37·35	37·30	36·67	38·04	38·34	38·30	35·96	37·17
TiO_2	5·28	3·01	3·39	3·05	3·46	3·60	5·32	3·14
Al_2O_3............	15·82	16·52	17·10	18·11	11·92	13·99	14·36	14·60
Fe_2O_3.........	4·42	3·36	4·58	3·64	7·74	3·98	1·42	3·75
FeO	15·43	16·89	16·36	15·36	17·92	20·24	26·16	26·85
MnO	0·02	0·05	0·04	0·05	0·04	0·09	0·04	0·06
MgO	10·25	11·02	9·20	10·52	9·66	7·96	5·59	4·23
CaO	1·30	2·60	0·38	1·52	0·44	0·90	0·54	0·17
Na_2O............	0·52	0·48	0·21	0·70	0·51	0·50	0·53	0·15
K_2O	8·16	7·18	9·17	7·36	8·36	8·31	8·62	8·25
H_2O+	0·60	1·36	1·98	1·48	1·46	1·63	1·10	1·35
H_2O-	...	...	...	...	...	...	...	...
F..................	1·25	0·22	1·37	0·07	0·58	0·32	0·21	0·85
BaO	...	...	...	...	...	0·02	...	...
SrO	...	...	...	...	...	none	...	...
	100·40	99·99	100·45	99·90	100·43	99·84	99·85	100·57
Less O=F......	0·53	0·09	0·57	0·03	0·24	0·13	0·09	0·36
Sum	99·87	99·90	99·88	99·87	100·19	99·71	99·76	100·21
K	3·2	2·8	3·5	2·9	3·3	3·3	3·6	3·3
Na	0·3	0·3	0·1	0·4	0·3	0·3	0·4	0·1
Ca	0·4	0·9	0·1	0·5	0·1	0·1	0·2	0·1
Mg............	4·7	5·1	4·1	4·8	4·5	3·7	2·7	2·0
Fe″............	4·0	4·4	4·1	3·9	4·7	5·3	7·1	7·2
Al	1·1	1·5	1·2	2·1	0·3	1·3	1·2	1·3
Fe‴	1·0	0·8	1·1	0·8	1·8	1·0	0·3	0·9
Ti	1·2	0·7	0·8	0·7	0·8	0·9	1·3	0·8
Si	11·4	11·5	11·1	11·6	11·9	12·1	11·7	11·8
Al	4·6	4·5	4·9	4·4	4·1	3·9	4·3	4·2
O	40·0	40·0	40·0	40·0	40·0	40·0	40·0	40·0
O	4·4	4·8	1·4	4·9	3·9	4·3	4·5	3·4
OH............	1·2	2·8	4·0	3·0	3·0	3·0	2·4	2·9
F...............	2·4	0·4	2·6	0·1	1·1	0·3	0·4	1·7
α...............	1·602	1·608	1·604	1·588	1·598	1·608	1·602	1·610
β...............	1·663	1·665	1·656	1·648	1·655	1·666	1·670	1·676
γ...............	1·664	1·665	1·656	1·648	1·655	1·666	1·673	1·677
2V............	5	3	0	0 to 5	3	2	12	5
Disp.	r < v weak	r < v perc.	r < v perc.	r < v perc.	r < v perc.	r < v perc.	r < v very strong	r < v strong
α...............	Pale yellow-brown	Pale yellow-brown	Pale brown	Pale yellow-brown	Pale brown	Pale brown	Pale yellow-brown	Pale brown
$\beta + \gamma$	Dark brown	Dark olive-brown	Dark brown	Dark brown	Dark brown	Dark green-brown	Dark brown	Dark brown
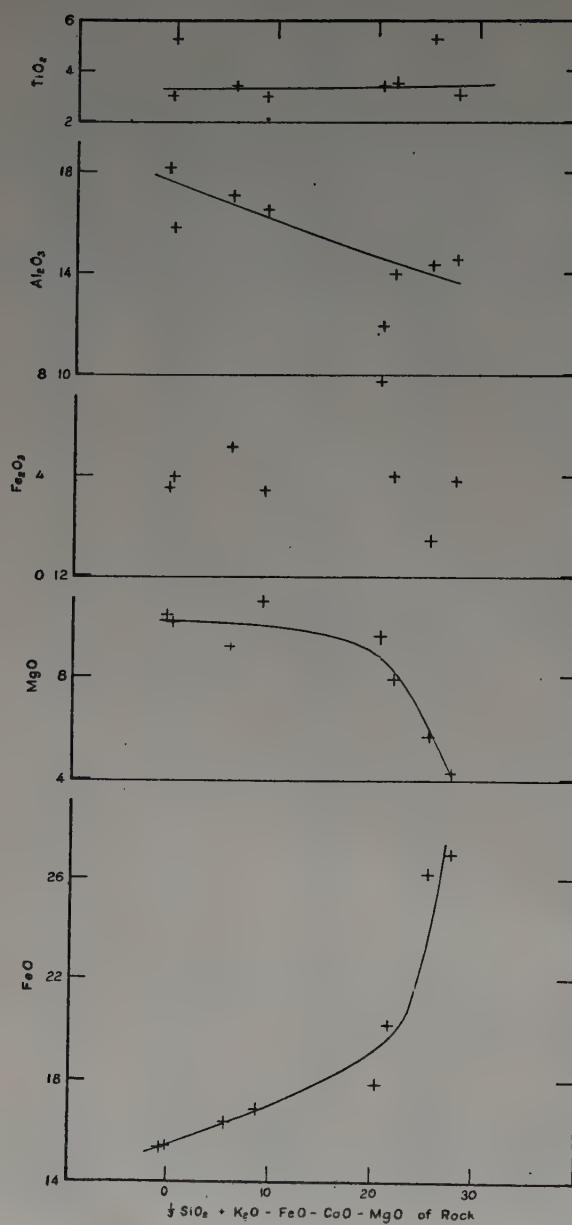
FIG. 2.—*Compositions of biotites plotted against position on the variation diagram of the enclosing rock.*
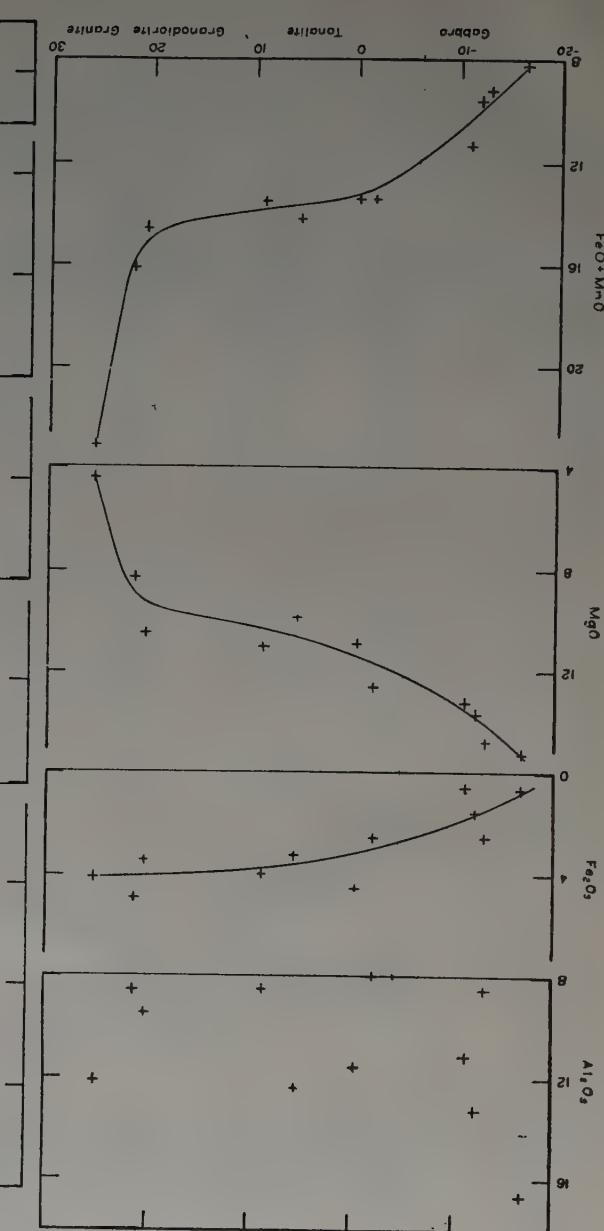
FIG. 3.—*Compositions of the amphiboles plotted against position on the variation diagram of the enclosing rock.*

TABLE 3. *Analyses and other data on Amphiboles*

	1	2	3	4	5	6	7	8	9	10	11
SiO_2	44·71	48·55	45·19	48·17	47·81	43·92	46·62	43·72	45·19	45·93	39·56
TiO_2	0·63	0·97	2·06	0·57	1·26	1·54	1·34	1·44	1·70	1·14	1·46
Al_2O_3	16·76	8·57	13·42	11·18	7·96	11·60	8·46	12·40	9·48	8·53	12·18
Fe_2O_3	0·72	2·60	1·58	0·61	2·61	4·58	3·96	3·32	3·46	4·92	4·10
FeO	8·22	9·15	9·62	11·33	13·34	13·36	13·54	14·22	14·50	16·15	23·18
MnO	0·11	0·09	0·09	0·08	0·08	0·11	0·07	0·07	0·07	0·29	0·09
MgO	15·30	14·81	13·72	13·37	12·65	10·87	10·99	9·86	10·48	8·28	4·43
CaO	10·39	12·59	11·17	11·69	11·40	10·80	11·58	11·64	11·52	10·97	9·98
Na_2O	1·72	0·99	1·55	0·91	1·16	1·24	1·16	0·86	1·45	1·22	1·81
K_2O	0·11	0·16	0·21	0·14	0·71	0·59	0·71	0·77	0·79	0·89	1·38
H_2O+	1·51	1·65	1·49	2·06	1·13	1·54	1·67	1·69	1·37	1·93	1·26
BaO	none	none	none	none	none	...	none	...	...	none	...
SrO	none	none	none	none	none	...	none	...	...	none	...
F	0·08	0·08	0·18	0·16	0·21	0·09	0·17	0·18	0·23	0·21	1·20
Sum	100·26	100·21	100·28	100·27	100·32	100·24	100·27	100·18	100·24	100·46	100·63
Less O=F	0·03	0·03	0·08	0·07	0·09	0·04	0·07	0·08	0·09	0·09	0·51
	100·23	100·18	100·20	100·20	100·23	100·20	100·20	100·10	100·15	100·37	100·12
Formulæ:											
Ca	3·20	3·90	3·50	3·60	3·60	3·40	3·70	3·70	3·70	3·50	3·30
Na+K	1·00	0·60	0·90	0·60	0·90	0·90	1·00	0·80	1·10	1·10	1·60
Mg	6·50	6·40	5·90	5·70	5·50	4·80	4·80	4·40	4·70	3·70	2·10
Fe	1·90	2·20	2·30	2·70	3·30	3·30	3·40	3·50	3·62	4·00	6·00
Mn	...	...	...	...	...	...	...	...	...	0·10	...
Fe'''	0·20	0·60	0·40	0·10	0·60	1·00	0·90	0·70	0·80	1·10	1·00
Al	2·34	0·90	1·60	1·60	0·90	1·20	0·60	1·20	...	0·30	0·60
Ti	0·10	0·20	0·50	0·30	0·30	0·30	0·40	0·30	0·40	0·30	0·30
Al	3·30	2·00	3·00	2·20	1·90	2·90	2·30	3·10	3·30	2·30	3·80
Si	12·71	14·00	13·00	13·80	14·10	13·10	13·70	12·90	13·50	13·70	12·20
O	22·00	22·00	22·00	22·00	22·00	22·00	22·00	22·00	22·00	22·00	22·00
OH	2·90	3·20	2·90	3·90	2·20	3·10	3·30	3·50	2·70	3·80	2·60
F	0·10	0·10	0·20	0·10	0·20	·20	0·20	0·40	0·40	0·20	2·3
O	1·00	0·70	0·90	0·90	1·60	0·70	0·50	0·10	0·90	...	... 0
Sp. G.	3·17	...	3·17	3·15	3·28	3·21	3·29	3·26	3·51	...	3·42
α	1·646	1·638	1·661	1·648	1·655	1·668	1·661	1·667	1·667	1·670	1·690
β	1·653	1·654	1·669	1·664	1·670	1·677	1·673	1·680	1·678	1·680	1·702
γ	1·668	1·668	1·678	1·678	1·680	1·683	1·679	1·685	1·685	1·687	1·711
2V	(+)82	(−)79	(−)80	(−)81	(−)66	(−)66	(−)56	(−)60	68	(−)57	(−)55
Disp.	r<v	r<v	r<v	r<v	r<v	r>v	r>v	r S v	...	r>v	weak
Z∧c	17½	14	18	13½	16	20	22	11	17	14	15
α	Pale yellow-green	Pale greenish yellow	Pale yellow-brown	Pale yellow-brown	Pale yellow-green	Light greenish yellow	Yellow-green	Yellow-green	Light tan-green	Pale yellow-green	Yellow-brown
β	Pale olive	Olive-green	Greenish brown	Olive-green	Olive-green	Olive-green	Olive-green	Olive-green	Olive-green	Green brownish cast	Grey-green
γ	Pale blue-green	Deep blue-green	Deep olive-green	Deep blue-green	Dark olive-green	Dark olive-blue	Deep olive-green	Dark blue-green	Dark olive-green	Dark blue-green	Olive-green
	Reaction on olivine	Hydroth. fibrous	Poikilitic	Hydroth.	Reaction	Coarse	Reaction	Grains	Grains	Grains	Grains
Rock	Troctolite	Calcic hornblende gabbro	Calcic hornblende gabbro	Calcic uralite gabbro	Norite nodule	Bonsall tonalite	Green Valley tonalite	Lakeview tonalite	Bonsall granodiorite	Woodson granodiorite	Granite
	SLR M354	SLR M30	SLR M108	SLR M53	SLR M229B	SLR 1016	SLR 138	EL 38-134	SLR 2242	Ra 135	E138-167

1. Hornblende formed from reaction on olivine from olivine-hornblende troctolite (SLR M354) north-east end of summit ridge of Pala Mountain. Plagioclase is An_{94}.

2. Light green uralitic hornblende from a calcic hornblende gabbro (SLR M30). Plagioclase is An_{98}. From north-eastern part of San Luis Rey quadrangle, road half-mile north of Magee ranch.

3. From calcic hornblende gabbro (SLR M108). From central summit of Pala Mountain. Plagioclase is An_{90}.

4. Bright green uralitic hornblende. From a calcic hornblende gabbro (SLR M53). Plagioclase is An_{88}. Near Pala. Head of main gulch on west side of Pala Chief Hill at an altitude of 1,400 feet.

5. Matrix of nodular gabbro (SLR M229B). About $0\cdot5$ miles east of Inland Highway at Vista Grande. Gabbro is made up of closely spaced nodules of pyroxene rock imbedded in a matrix of hornblende rock. Plagioclase is An_{50}.

6. From Bonsall tonalite (SLR 1016) from Rincon grade. Has large oikocrysts of hornblende. Plagioclase is An_{47}.

7. Hornblende with well crystallized borders and cores of uralitic hornblende. From Green Valley tonalite (SLR 138) two miles north-west of the south-east corner of the San Luis Rey quadrangle. Plagioclase is An_{85}. Analysis is of well-crystallized borders.

8. From Lakeview tonalite (El 38–134) four miles north-east of Perris. Plagioclase is An_{85}.

9. Hornblende from a granodiorite variety of the Bonsall (SLR 2242). One mile west of Fallbrook. Plagioclase is An_{32}.

10. Hornblende from Woodson Mountain granodiorite (Ra 135) from near top of Poway grade in Ramona quadrangle. Plagioclase is An_{85}.

11. Hornblende from coarse granite of Rubideaux Mountain, Riverside, California. Plagioclase is An_{20}.

In Figure 3, the compositions of the amphiboles are plotted against the positions of the rocks in which they occur on a variation diagram ($1/3\ SiO_2 + K_2O - FeO - MgO - CaO$). This figure and Table 3 show that, except for the low SiO_2 and high K_2O and F in the amphibole from the granite, SiO_2, TiO_2, the alkalies, H_2O, F, and CaO have a moderate range and without obvious relation to position on the plot. TiO_2 and alkalies are rather low; Al_2O_3 covers a wide range and is very high in the hornblende formed from reaction between olivine and plagioclase (anal. 1). Fe_2O_3 is low in the hornblende from the gabbros, and is moderate in those from the granites and granodiorites. FeO ranges from 8 to 10 per cent in the amphiboles from the gabbros and is over 23 per cent in that from the granite. The curve for iron has two prominent inflections. The MgO varies inversely with the FeO.

The amphibole represented by analysis 1, Table 3, was formed by reaction between olivine and a calcic plagioclase (An_{94}). Its norm is:

or	$0\cdot56$	di	$10\cdot90$
ab	$12\cdot58$	ol	$33\cdot56$
an	$38\cdot09$	mt	$0\cdot93$
ne	$0\cdot85$	il	$1\cdot22$

This amphibole could be made from a mixture of about 51 per cent of An_{94} and 36 per cent of olivine, with the addition of some H_2O, CaO, alkalies and SiO_2.

PLAGIOCLASE

The plagioclases of the rocks range in anorthite content from 94 in the calcic gabbros to 18 in the granites. The plagioclase in the microperthite is more sodic. Miller (1937, p. 1414) made a statistical study of the composition of the plagioclase in the San Marcos gabbro and found in the rocks with olivine and pyroxene pronounced concentrations of the feldspar at anorthite contents 93, 60 and 53. In the hornblende rocks he found the three concentrations at 90, 57, and 49.

The plagioclases change rather regularly with the composition of the enclosing rock, as shown in Figure 4. In this figure about 75 per cent of the plagioclases fall on a smooth curve within the limit of error of the determinations ($\pm$ 3 per cent An). The other points all have low anorthite content and only one is off the curve by more than 8 per cent anorthite. This rock fails to fit the variation curve and is very low in CaO and MgO and high in FeO and Na_2O.

Four plagioclases from rocks ranging from calcic gabbro to granodiorite have been analysed by F. A. Gonyer and are listed in Table 4. They contain small amounts of Fe_2O_3 and K_2O and the K_2O and probably the Fe_2O_3 increase with the soda content.
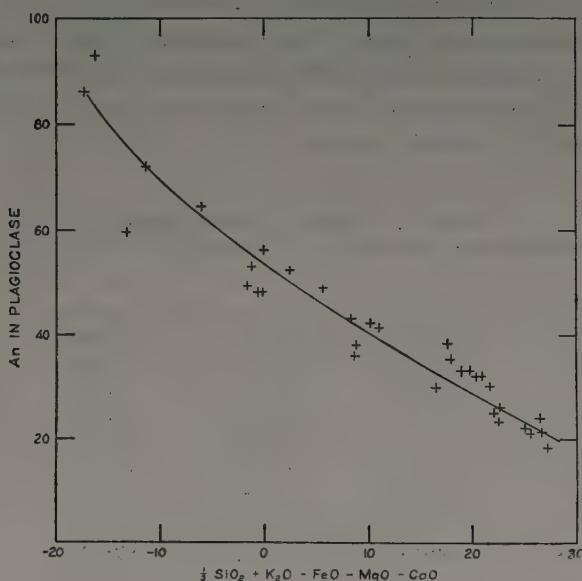
FIG. 4.—*Anorthite content of plagioclase plotted against position on the variation diagram of the enclosing rock.*

TABLE 4.   *Analyses of Plagioclase*

	1	2	3	4
SiO_2	43·77	52·97	57·20	63·40
Al_2O_3	36·11	29·41	26·80	22·20
Fe_2O_3	0·09	0·76	0·50	1·00
MgO	0·07	...	...	...
CaO	18·73	12·59	8·50	3·60
Na_2O	0·67	3·97	6·30	9·20
K_2O	0·11	0·26	0·50	0·50
H_2O	0·40	0·22	0·20	0·10
Sum	99·95	100·18	100·00	100·00
Or	0·60	1·80	3·40	3·40
Ab	5·80	34·70	54·30	78·20
An	93·60	63·50	42·30	18·30

1. Plagioclase from calcic gabbro (SLR 354). North-east end of summit ridge of Pala Mountain.

2. Plagioclase from typical norite of San Marcos gabbro (SLR M334). Summit of San Marcos Mountains, at BM 1664, three miles east of Vista.

3. Plagioclase from Bonsall tonalite (El 38–28). Shaft 2, two miles west of Valverde. The analysis is corrected for 7·5 per cent of quartz.

4. Plagioclase from Woodson Mountain granodiorite (SLR 596). Half a mile east of Rainbow. Analysis is corrected for 9·5 per cent of quartz.

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ORTHOCLASE, MICROCLINE, AND PERTHITE

Small amounts of these minerals are present in the silica-rich tonalites and they are uncommon in rocks with less than 25 per cent of quartz. Much of the potash-feldspar is microcline microperthite.

Chemical analyses of four perthites and alkali determinations on two others have been made by F. A. Gonyer and the results are given in Table 5.

TABLE 5. *Analyses of Potash-feldspars*

	1	2	3	4	5	6
SiO$_2$	63·88	63·96	64·26	63·48	...	...
Al$_2$O$_3$	17·92	19·12	19·14	19·26	...	...
Fe$_2$O$_3$	0·64	0·32	0·38	0·32	...	...
CaO	0·52	0·34	0·26	0·22	...	...
Na$_2$O	2·71	1·77	2·01	1·44	3·48	2·88
K$_2$O	12·09	13·32	13·30	14·30	10·62	12·36
H$_2$O	0·72	0·26	0·37	0·40	...	...
Sum	98·48	99·09	99·72	99·42	...	...
Or	74·30	82·30	81·00	86·60	67·00	74·00
Ab	23·70	16·00	17·50	12·30	31·00	25·00
An	2·00	1·70	1·50	1·10	...	...

1. From Green Valley tonalite (SLR 685). South of Vista, in upper part of Los Monos Canyon. Rock contains 10 per cent of perthite.

2. Large glassy feldspar from the coarse granodiorite (El 38–126) associated with the Bonsall tonalite. East portal of tunnel five miles north-east of Perris. Rock contains 14 per cent of orthoclase.

3. From a granodiorite facies of the Bonsall tonalite (SLR 2242). One mile south-west of Fallbrook. Contains 14 per cent perthite.

4. From the Woodson granodiorite (SLR 596) from a small quarry east of Rainbow, San Luis Rey quadrangle. Rock contains 22 per cent of perthite.

5. From coarse granite of Rubideaux Mountain (El 38–167) near Riverside, California. Rock contains 32 per cent microperthite.

6. From the fine granite of Rubideaux Mountain, Riverside, California. Rock contains 36 per cent of microperthite.

THE RATIO OF IRON TO MAGNESIA IN THE ROCKS AND MAFIC MINERALS

The ratio (weight per cent) of $\dfrac{FeO + MnO}{FeO + MnO + MgO}$ and $\dfrac{FeO + Fe_2O_3 + MnO}{FeO + Fe_2O_3 + MnO + MgO}$ for the analysed rocks and minerals is plotted against the position on the variation diagram in Figure 5. The figure shows that for any rock the ratios are nearly the same for the rock and for all the mafic silicates in the rock, and that the ratio $\dfrac{FeO + MnO}{FeO + MnO + MgO}$ is about 37/100 in the mafic gabbros and increases as the SiO$_2$ of the rock increases and is 85/100 in the granites. The slope of the curve for this ratio is not regular but is flat in the range of the tonalites and steep in that of the granodiorites and granites. The points for the rocks near the granite end are not very accurate as the amounts of FeO and MgO are very small.

The ratios for the amphiboles tend to be a little lower than those of the rocks or of the biotites. Those for the biotites and hypersthenes are near those for the rocks.

If Fe$_2$O$_3$ is included in the ratio, the points fall near a more regular curve.

Comparison of the Batholith of Southern California with the Lavas of the San Juan Mountains of Colorado

Some of the ways in which the granular rocks of Southern California differ from those of the San Juan lavas are:
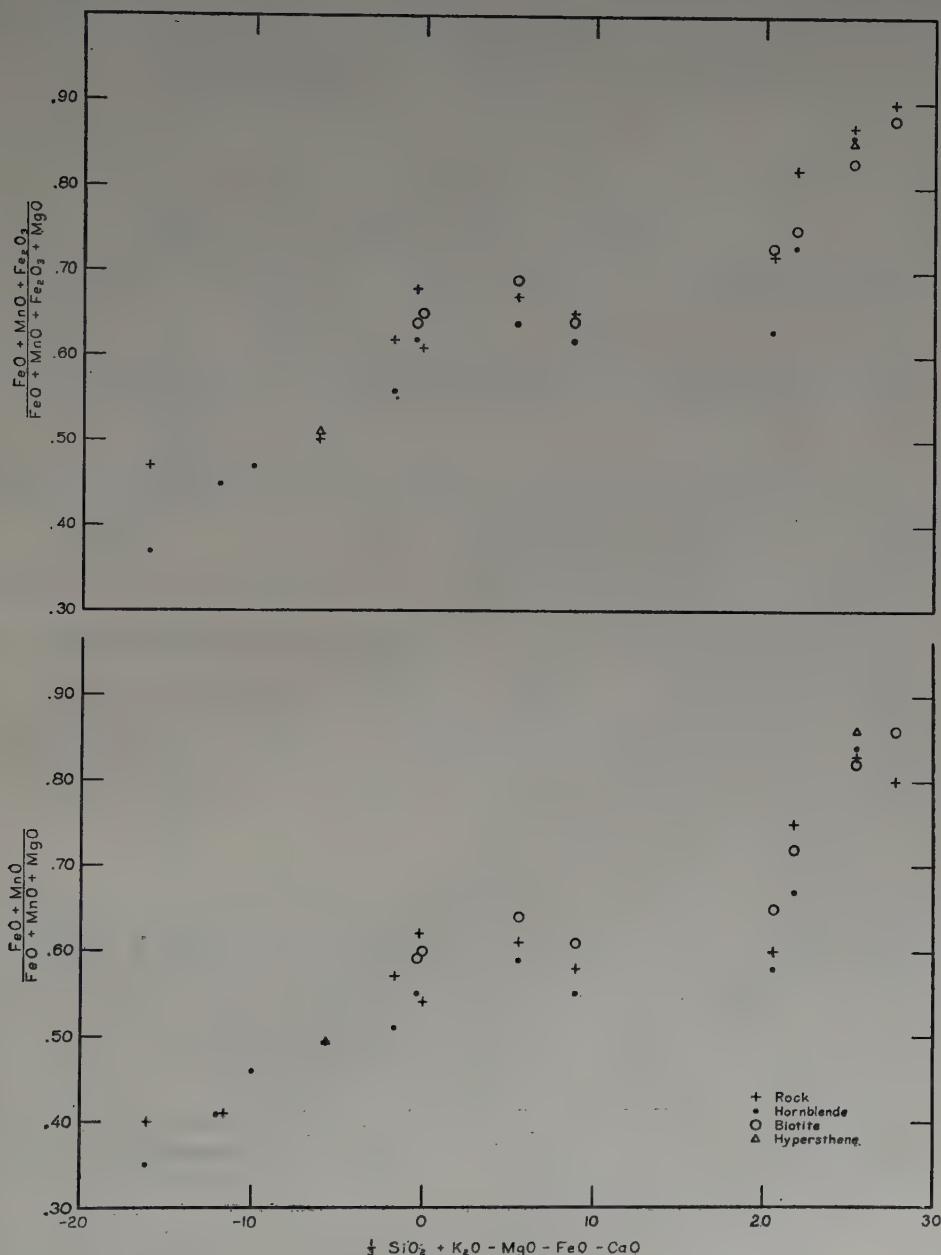
FIG. 5.—Ratio of $\dfrac{FeO + MnO}{FeO + MnO + MgO}$ and $\dfrac{FeO + Fe_2O_3 + MnO}{FeO + Fe_2O_3 + MnO + MgO}$ of the mafic minerals and the enclosing rocks, plotted against the position of the rocks on the variation diagram.

1. The lavas of the Potosi volcanic series of the San Juan mountains contain more K_2O than do the granitic rocks of Southern California. As a result, rocks with the composition of tonalites and diorites are entirely absent from the San Juan lavas. The range in rocks for the two groups is shown in Figure 6, in which the abscissa is the position on the variation diagram used in this paper.
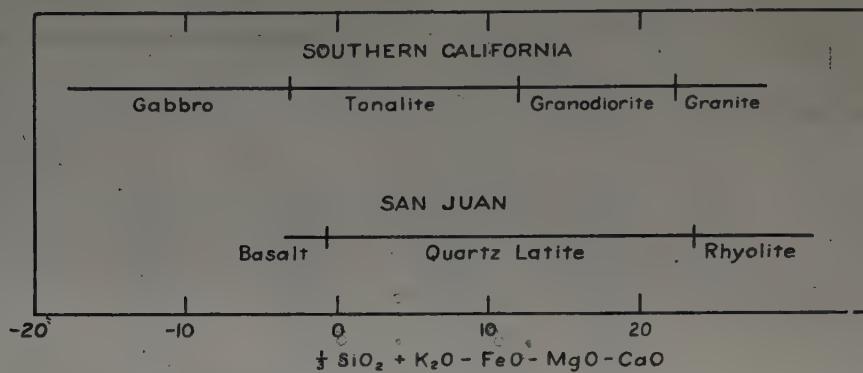
FIG. 6.—*The range in rocks in the batholith of Southern California and in the Potosi volcanic series of the San Juan Mountains of Colorado.*

2. For the granular rocks, except in the very late part, the crystallization was approximately under equilibrium conditions while in the lavas this was far from true for the groundmass and was probably not true even for the phenocrysts.

3. Foreign crystals picked up by the granular rocks were in large part reworked by the magma while this is less true of the lavas.

4. Important recrystallization took place in the granular rocks during the last or deuteric stage of crystallization while little took place in the lavas.

5. Escape of mineralizers near the surface from the lavas brought about reactions such as the resorption of biotite and amphibole and oxidation of the iron in these minerals, but such effects were not observed in the granular rocks.

The minerals of the granular rocks of Southern California and the phenocrysts of the San Juan volcanics are compared diagrammatically in Figure 7.

In the granular rocks, olivine is found only in rocks without quartz or normative quartz, but in the lavas olivine phenocrysts are present with quartz phenocrysts and in rocks with as much as 15 per cent of normative quartz. The olivines of both rocks have about 25 per cent of fayalite.

In the granular rocks, pyroxene is absent in a few of the very calcic gabbros, it is the chief dark silicate in most of the gabbros, it ends rather abruptly at position O on the variation diagram, it is absent in the tonalites and granodiorites, and as hypersthene comes in again in a few of the granites. Rather different relations were found in the lavas where pyroxene and olivine are the only dark silicates in the basalts and silica—poor quartz latites—as far as position O on the variation diagram. At about that position, hornblende and biotite appear but augite is present in many of the rocks to the right of the position named and continues as a phenocryst to the potash-rich rhyolites.

Hornblende has about a reciprocal relation to pyroxene. In the granular rocks it is present in variable amounts as a late mineral in many of the gabbros, even in the highly calcic gabbros. At about position O where pyroxene ends, hornblende becomes the chief dark silicate and crystallized rather early. As the rocks become rich in SiO_2, both the absolute amount of hornblende and its proportion in the dark silicates decreases and it is in minor amount or absent in the granites. In the volcanic rocks hornblende is rarely the chief dark mineral.

The distribution of biotite is much the same in both the granular and the volcanic rocks. It is absent in the gabbros and basalts and comes in with quartz in both groups, at about position —2.
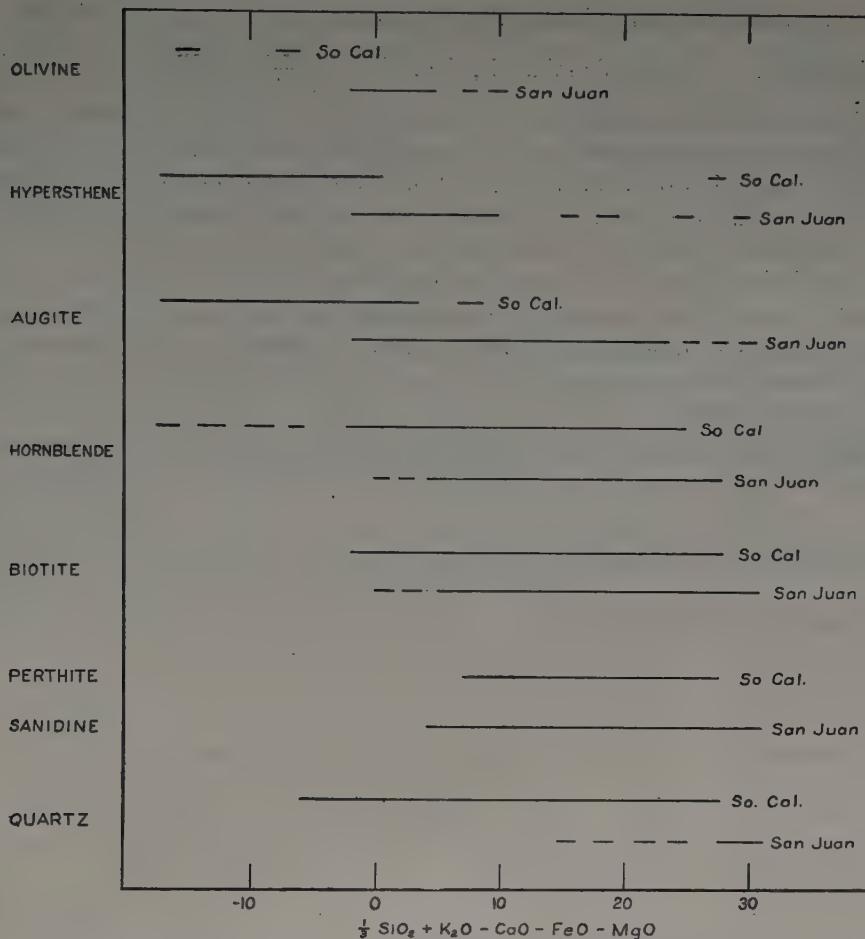
FIG. 7.—*The minerals of the granitic rocks of Southern California and the phenocrysts of the Potosi rocks of the San Juan Mountains of Colorado.*

In the granular rocks it is the chief dark mineral at about position 5 and in the volcanic rocks at position 12. In both groups it forms a small part of the dark silicates in the silica-poor rocks, but this part increases with increase of silica, and biotite is the chief dark silicate in the granites and rhyolites.

In all the granular rocks plagioclase is an abundant mineral and it ranges from An_{94} in the calcic gabbros to An_{18} in the granites. The differentiation has not gone far enough to yield kaligranites. In a few of the rocks some of the plagioclase has very calcic cores, representing foreign crystals not completely reworked. Except for this, zoning in the plagioclase is uncommon, and where present is in broad zones with little recurrent zoning, and progressing from calcic cores to sodic borders. In the volcanics plagioclase phenocrysts are present in nearly all the rocks, except the kalirhyolites in which there is very little lime for anorthite. It is rarely more sodic than An_{18} and there appears to be a reaction relation between plagioclase and sanidine. Both calcic and sodic cores are rather common and are relics of foreign crystals. Zoning is conspicuous in many of the plagioclases and is commonly recurrent and complex.

In the granular rocks microcline microperthite is the common potash feldspar and it is for the most part interstitial. It is rare in rocks with less than 10 per cent of normative orthoclase. In the lavas sanidine phenocrysts are common in many rocks with over 23 per cent of normative orthoclase.

In the granular rocks the compositions of all the minerals change regularly with the composition of the enclosing rocks. For the mafic minerals, the ratio $\dfrac{FeO + MnO}{FeO + MnO + MgO}$ is ·38 in the calcic gabbros and increases along a smooth curve with inflections to ·85 in the granular rocks (Figure 5). In the lavas there is no apparent relation between the ratio for the minerals and the composition of the enclosing rock, and all of the mafic minerals of the lavas contain only a moderate amount of iron. In biotites of the granular rocks there is commonly over three times as much FeO as Fe_2O_3 and in the amphiboles even more, yet in some of those minerals from the volcanics, the iron is mostly in the ferric state. The biotites of the lavas contain less K_2O than do those of the granular rocks.

The anorthite content of the plagioclase of the granitic rocks decreases regularly as the host rock changes from calcic gabbro to granite (Figure 4), but those of the San Juan volcanic rocks are much more erratic. The plagioclase phenocrysts of the lavas contain more K_2O than do those of the granular rocks of Southern California.

The sanidines of the lavas carry much more soda than do the microperthites of the granular rocks.
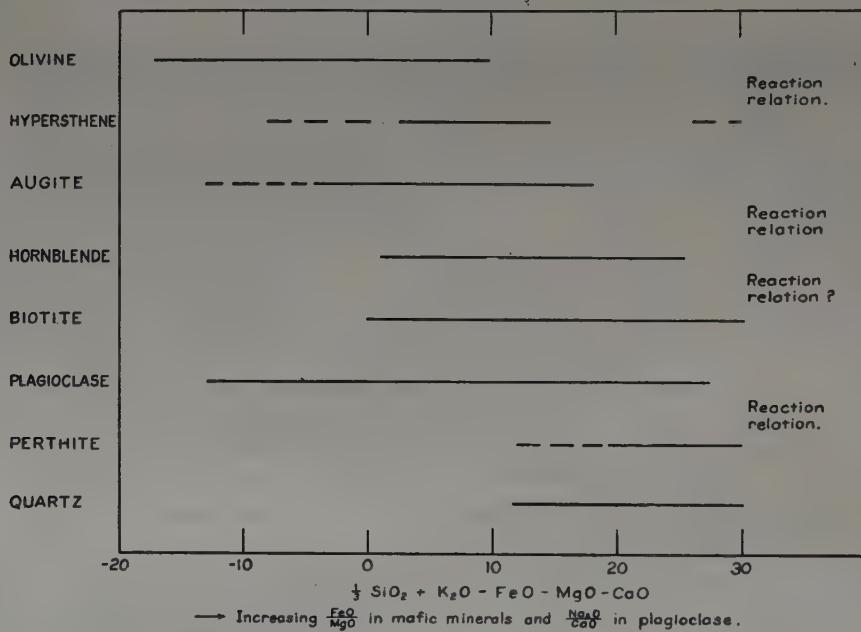

FIG. 8.—*The crystallization of the batholith of Southern California.*

CRYSTALLIZATION OF THE MAGMA AND REACTION SERIES

Olivine, probably accompanied by calcic plagioclase and pyroxene, was the first constituent to crystallize from the calcic gabbro and olivine continued to crystallize until the residual liquid contained 10 or 15 per cent of excess SiO_2. It was then reacted on to form pyroxene. Both pyroxenes crystallized until the liquid had some excess of SiO_2, augite probably a little longer than hypersthene. They were then reacted on to form biotite and hornblende. Biotite continued to the end while hornblende dropped out in the granites. An iron-rich hypersthene may have replaced the hornblende. Quartz and perthite crystallized together in the residual liquid; in the California batholith quartz preceded perthite, but in the potash-rich lavas of the San Juan region sanidine preceded quartz.

There is no evidence of a reaction relation between hypersthene and clinopyroxene and doubtful evidence for that between hornblende and biotite. No appreciable amount of quartz can be formed by

reaction. In the San Juan lavas there is evidence for the reaction on plagioclase to form sanidine. As the soda content of the plagioclase increases the iron content of the mafic minerals also increases.

The mineralizers have some influence on the reactions. The hornblende in the gabbros of Southern California are late reaction or deuteric minerals and in part, at least, replace pyroxene and are formed by reaction between olivine and calcic plagioclase. On the other hand, in some of the volcanics of the San Juan loss of mineralizers resulted in reaction on hornblende and biotite to form pyroxene.

The course of crystallization and reaction is represented approximately in Figure 8.

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SOME APPLICATIONS OF AUTORADIOGRAPHY

By J. P. MARBLE

U.S.A.

ABSTRACT

A properly prepared surface of a radioactive mineral, when placed in direct contact with a photographic plate or film for an optimum time will yield valuable information as to relative radioactive content of different parts of the specimen, leaching, infiltration of radioactive matter, movements subsequent to original crystallization, and other points. In some cases the existence of the metamict condition can be determined. By exposing for the same length of time chips of an unknown mineral with others whose U+Th content is known, a semi-quantitative estimate of the U+Th content of the unanalyzed mineral can be quickly made.

EVER since the discovery of the effect of uranium minerals on a photographic plate by Henri Becquerel in 1896* the autoradiograph has been used to illustrate the effect in elementary courses in physics, and in popular magazine articles. The mineralogist has also applied the process (1) to detect the presence of radioactive minerals in a sample; (2) to locate in a given specimen small particles of radioactive minerals accompanied by inert substances; (3) in a roughly qualitative way to estimate the amount of uranium and thorium present; and (4) to study the " freshness " of the radioactive mineral, i.e. the amount of leaching or enrichment as shown by variations in the blackening of the plate.

Most of this work has been done in a rather desultory fashion, and only in the last few years (excluding the war period) has there been much attempt to systematize the results. Very recently H. Yagoda of the United States National Institute of Health, Bethesda, Maryland, U.S.A. has been making careful, quantitative studies of the effect of radioactive minerals on the photographic emulsion, on the use of the relative darkening of the plate as a means of the quantitative estimation of the radioactive content, and on the detection of natural radioactivities other than uranium and thorium. (Yagoda, 1943, 1946, 1947.)

In this work, which is still in progress, and part of which will be illustrated later, the writer has been co-operating.

Geologists and geochemists in general, however, do not seem to be familiar with the simple techniques involved, and by no means all mineralogists; nor with the amount of information that can be obtained. The writer outlined briefly at the Seventeenth Congress (Marble, 1937), some work of his on allanite, but it is felt that a wider discussion may be of some interest.

For quantitative or semi-quantitative work the one essential is that the surface of the specimen in contact with the emulsion be flat. A sawed section for a large specimen, or a cleavage surface or crystal face, for a small one, should be ground as flat as possible on a lap, using progressively finer abrasives. An optical polish is not needed, and it is the experience of the writer that a highly polished surface tends to be less plane because of the varying hardness of the different minerals. Further, polishing tends to obscure weathered zones because of the dragging out of the more friable material and its replacement by the very fine particles of the polishing materials. Excess abrasive can be removed from cracks by brushing gently under water or alcohol, the choice of liquid depending upon circumstances. Especial care should be taken when friable weathering or alteration products or secondary minerals are present. It is advisable to leave the specimen in the dark or in any event unexposed to

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*See BECQUEREL, J. *Nature*, vol. clxi, p. 609 (1948), for a discussion of the circumstances surrounding Becquerel's discovery.

intense light (especially ultraviolet) for an hour or so before starting the radiograph. This will avoid the possibility of reaction between the emulsion and fluorescent substances (which may not be radio-active) in the specimen.

For most purposes the choice of emulsion and backing is not critical. Eastman or other " process " films or plates give good results. A glass plate is perhaps preferable to a film when exposures of several weeks are necessary, as changes in temperature or humidity may cause a film to buckle slightly. Heavy (500+ gram) specimens should have the emulsion in contact with an upper surface, to avoid possible pressure effects. This precaution is advisable when the radioactive content is extremely small. Yagoda recommends Eastman Special Alpha-particle Emulsion for quantitative estimation. Development should be carried out to the point of maximum contrast, care being taken not to lose detail.

The time of exposure will of course, depend upon the total radioactivity of the material. The non-radioactive matter present has considerable effect, as the absorption of radiation is a quantity that varies from ion to ion. Thorium, whose net radioactivity is weaker than that of uranium, requires a longer exposure. The Table printed below may be used as a rough guide.

TABLE I

Suggested Exposure Times for varying Radioactive Content

Minerals containing 25 per cent U+Th or over .... 48 hours
Minerals containing 10–25 per cent U+Th .... 1 week
Minerals containing 5–10 per cent U+Th....................... 2 weeks
Minerals containing 1–5 per cent U+Th .... 3 to 4 weeks
Minerals containing less than 1 per cent of U+Th .... 4 to 6 weeks
The lower useful limit is about ½ per cent Th or its equivalent.

Minerals, such as samarskite and its congeners, which are in the metamict state sometimes give abnormal pictures. A " spotty " effect may be found where a considerable proportion of the radio-activity appears to be localized against a uniform fainter background. Yagoda attributes this to the formation of radiocolloids, where radium as such is concentrated. He is continuing work on this phenomenon.

In interpreting the radiographs, it will be found often that the outline on the plate is slightly larger than the surface of the mineral in contact with the plate, and that the outline is somewhat " fuzzy." This is usually due to alpha-particles that have been emitted from the sides of the specimen and have travelled to the emulsion before reaching the end of their air-range. If the outline of the image is much blurred, the cause is probably either over-exposure, or movement of the specimen on the plate.

Parenthetically we may remark that the techniques above outlined do not apply to the problem of the radioactive content of rocks, except for those containing visible (under the binocular microscope) amounts of minerals of reasonably high radioactive content. The general problem of the photographic determination of the total radioactive content of rocks as such, and the localization therein of the radioactive elements has been recently discussed by Mme. Joliot-Curie (1946), and very recently tested, with interesting results by Poole and Bremner (1948).

DESCRIPTION OF PLATES

Some typical effects may be seen in the figures on Plates I and II.

Fig. 1 (*Pl. I*) shows one medium-sized and several small fragments of a non-radioactive mineral (hornblende) included in an otherwise homogeneous allanite mass from Friar Mountain, Amherst County, Virginia, U.S.A. In the hand specimen they are somewhat difficult to distinguish. Exposure—3 weeks. Analysis: U = 0·08 per cent; Th = 1·25 per cent.

Fig. 2 (*Pl. I*), a 1-week exposure of a fragment of a monazite crystal—incidentally from the largest single crystal of monazite on record—from Mars Hill, North Carolina, U.S.A., shows a relatively uniform distribution of the radioactive content in the main mass, crossed in nearly opposite directions by two sets of fractures. Along one set Th + U have been leached out, along the other set they have

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been concentrated or introduced. It is difficult to say which set is the earlier, but there have been two periods of movement and circulation of waters since the mineral first crystallized. Analysis: U = 0·02 per cent; Th = 5·56 per cent.

Fig. 3 (*Pl. I*) is a 48-hour exposure of a specimen of pitchblende from No. 2 Vein, Eldorado Mine, Great Bear Lake, North West Territories, Canada, and shows a brecciated ore with inclusions of country rock. The pitchblende is apparently a late arrival, as in several places it surrounds other minerals without much replacement. The distribution of the radioactivity is quite uniform, showing the virtual absence of leaching and of secondary minerals. The original specimen was sawed in two, and both sides of the saw-cut ground flat. Analysis: U = 29·39 per cent; Th = <0·01 per cent.

Fig. 4 (*Pl. I*) is a 2-week exposure of an allanite from Rose Branch, Yancey County, North Carolina, U.S.A. The effect on the plate is barely visible.

Fig. 5 (*Pl. I*) is a 34-day exposure of the same sample. The following interpretation may be made. Allanite crystallized out from a solution of uniform composition for some time. Relatively suddenly the composition of the fluid altered, becoming more dilute in thorium. Leaching or other alteration followed, the second material being more readily subject to these processes. Finally fracturing occurred, with the introduction of non-radioactive material. Obviously a sample with such a complex history as this is, to say the least, of dubious value as material for an age determination by the Pb/U+Th method, so it was not analyzed. The Th content of the more uniform material is probably about 1 per cent. On the original specimen (of which a photograph has not yet been made) the difference between the two portions of allanite is not detectable.

Fig. 6 (*Pl. I*), a 1-month exposure of an allanite from Spruce Pine, North Carolina, U.S.A., shows material so badly leached, filled with non-radioactive material, and un-uniform in composition as to be worthless, either for age measurement, or for study as a sample of allanite. It is included as an horrible example.

Fig. 7 (*Pl. I*), made by Dr. Herman Yagoda, who has kindly permitted its reproduction, is an example of his technique. The lower left corner shows a bakelite mount containing several chips of minerals whose U + Th content is known from chemical analysis. The upper left corner is a similar mount of a fragment of allanite from Friar Mountain, Amherst County, Virginia, U.S.A.—not the same sample as in Fig. 1—showing " radiocolloids." The upper right corner is a mount containing some small chips of allanite from Greenwich, Massachusetts, U.S.A., which carry inclusions of quartz. The lower right corner carries two fragments of a very weakly radioactive, apparently not wholly homogeneous, allanite from Mount Adam, Rockland County, New York, U.S.A. Dr. Yagoda has estimated by photometric comparison with the " known " samples that the Greenwich allanite carries about $\frac{1}{2}$ per cent U or its equivalent. Chemical analyses by the writer, still in process, indicate 1·55 per cent Th + 0·09 per cent U, or a total of 0·65 per cent U equivalent.

Fig. 8 (*Pl. II*), a three-week exposure of three crystals of allanite from Whiteface Mountain, Essex County, New York, U.S.A., shows a relatively uniform distribution of the radioactive content, and a virtually complete absence of leaching, enrichment, fracture, or alteration products. The small specks may be " radiocolloids," but the material is reasonably anisotropic, so apparently not metamict. Analysis: U = 0·07 per cent; Th = 1·07 per cent.

Fig. 9 (*Pl. II*) is a 69-hour exposure of an uraninite with alteration products from Boqueirão, Rio Grande do Norte, Brazil. Four fragments of different size are present. Note that the uraninite either contains more uranium than the alteration products, or else that the alteration products contain ions having a greater absorptive power for alpha-radiation than does the unaltered uraninite. The alteration products have affected the plate to a lesser degree than the fresh mineral. Also note that it appears possible by careful picking to get unaltered material for analysis. This was successfully accomplished in actual practice. This uraninite contains 77·78 per cent U; 0·35 per cent Th.

The writer acknowledges the kindness and courtesy of the United States Geological Survey, the United States National Museum, and of Dr. Herman Yagoda of the National Institute of Health

for exposing and developing the original plates and making the original prints. Dr. Yagoda has also assisted in the interpretation of some of the features shown thereon. The analyses were made by the writer in the laboratories of the Survey and of the Museum.

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NOTE ADDED IN PROOF

Since this paper was delivered, Dr. Herman Yagoda has published a full account of the technique of mineral autoradiography in *Radioactive Measurements with Nuclear Emulsions* (Wiley, New York; Chapman and Hall, London, 1949). Interested workers should consult especially Chapters 3 and 7 of this authoritative work.

Fig. 1

PLATE I

Fig. 2

Fig. 3

Fig. 4
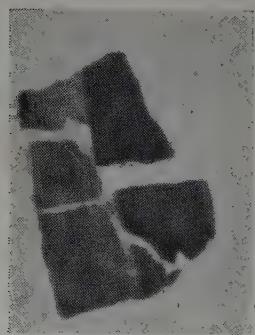
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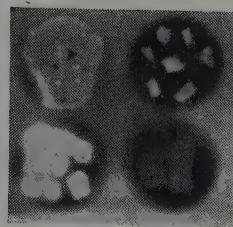
Fig. 7

Fig. 6
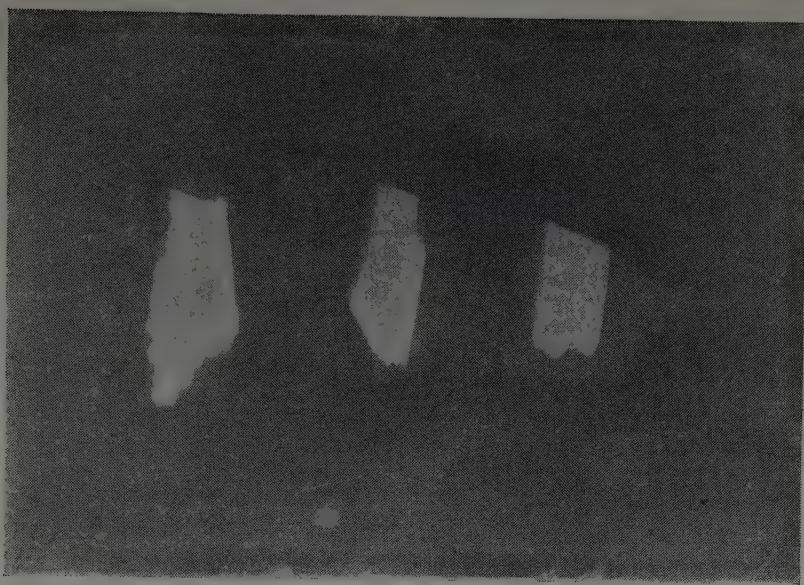
Fig. 8

Fig. 9

A GEOCHEMICAL METHOD OF
PROSPECTING FOR ORE DEPOSITS

By STANKO MIHOLIĆ
Yugoslavia

ABSTRACT

It has been shown elsewhere (*Economic Geology*, in print) that there is a certain parallelism between the geologic age of a system of joints and faults and the mineral deposits connected with them. In order to determine the age of such a system, the age of igneous rocks formed simultaneously is determined by a radioactive method. Besides the classical method based on the determination of uranium, thorium and lead, a much quicker and more convenient method based on the radioactive transformation of rubidium into strontium can also be used. When the age of the system is thus determined, the determination of heavy metals (other than iron and manganese) in mineral and thermal waters of the region gives an additional hint. The method has been applied with success in 1940 while prospecting for copper in Northwestern Croatia.

As known ore deposits are being depleted more or less rapidly, the task arises to discover new deposits in places where there are no visible outcrops. Several geophysical methods have been developed for this purpose and are widely used. Lately some geochemical, biochemical and geobotanical methods have also been described. There is still another geochemical method that might prove of some use, particularly in countries where the geological conditions are less well known. As has been shown elsewhere (Miholić, 1947) a certain parallelism exists between the geologic age of the joints and faults and the mineral deposits connected with them.

In order to determine the age of a system of joints and faults, the age of igneous rocks connected with them is determined by a radioactive method. Contrary to the current practice where generally radioactive minerals are isolated and their age determined, the author uses an average sample of the rock itself. This method has its advantages and drawbacks. The advantage is that the determined age shows a better average, while determinations of age on radioactive minerals have shown, that even different layers of the same crystal show a different age. The differences between the outer layer and the core of a crystal amount sometimes to 10 per cent (Alter and Yuill, 1937). The drawbacks on the other hand lie in the fact, that the elements relevant to the determination of age by radioactive methods as a rule occur in rocks only in very minute quantities and their analytical determination offers therefore considerable technical difficulties.

The author uses in his investigations two radioactive methods. There is first the well known " lead " method based on the determination of uranium, thorium and lead. Here particularly the determination of lead in rocks has proved difficult. The problem was solved by a very satisfactory polarographic method, already applied by the author in the determination of lead in mineral waters (Miholić, 1945). Owing to the very small amount of lead contained in the samples, no attempts have been made to determine the atomic weight of the lead thus isolated. F. E. Wickman (1943) however, has shown that the ensuing error due to pre-existent ordinary lead is not so great as to impair seriously the applicability of the method for the present purpose.

The second method applied by the author is a method developed by O. Hahn (1938) and based on the determination of the ratio Rb/Sr by a spectrographic method. This method is much quicker than the first one and allows a great number of determinations in a relatively short time. The method is however, comparatively new, yet undeveloped and applied hitherto but to a very small number of samples. Should it prove generally applicable it would become the method of choice. Detailed description of the technique employed in the determinations will be published shortly elsewhere.

When thus the age of a system of joints and faults is established, then the content in heavy metals in mineral (and especially thermal) waters of the respective region is determined. A polarographic method has proved very appropriate for this kind of work (Miholić, 1945). Mineral waters give usually a fair average of the mineralization of the deeper strata of the area under investigation.

The method has been applied practically in 1939-40 while searching for some ore deposits in Northwestern Croatia. On the northern foot and on the slopes of Mt. Ivančica there are two parallel faults. The northern one, stretching far to the West, is marked by a series of occurrences of andesites (Jesenje, Kameni Vrh, Laz, the Upper Valley of Bistrica) and dacites (Jesenje, Ves) (Gorjanović, 1904). Their petrography has been studied by M. Kišpatić (1909). The fault was formed during the Upper Jurassic or Lower Cretaceous (Poljak, 1942), but partly reactivated in Miocene. Along the fault there are occurrences of zinc ore (mainly smithsonite), particularly near Ivanec, where there are also traces of lead (Lipold, 1861). In the middle of the nineteenth century the deposits near Ivanec have been worked on a small scale for zinc, but the exploitation has long since been abandoned.

The southern fault, running higher up on the northern flank of Mt. Ivančica, is older and marked by effusions of melaphyres (Mt. Očura, Gečkovec, Topolje, the Upper Valley of Željeznica) (Gorjanović, 1904). The rocks are less well known and the exact age of the fault has not yet been determined.

The mineral waters connected with this system of faults, as far as they have been investigated (Dobrna, Gabernik, Kostrivnica) contain the following heavy metals (in decreasing quantities): zinc, lead and copper. No deposits of copper were known to exist. Still the age of the southern fault and the content of copper in the mineral waters connected with the faults indicated a possibility of such occurrences. Searches were made therefore along the southern fault line. Finally at Mt. Očura limonites were found containing 0,20—1,12 per cent of Cu. The enemy invasion of the country in 1941 stopped further work, which has not yet been resumed.

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SERPENTINES ET SERPENTINISATION

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ABSTRACT

The serpentines have generally a mesh texture and rarely fibrous lamellar (felted), serpophitic, spherulitic and semi-spherulitic texture.

Among the essential serpentinous minerals it has been possible to classify the following types: (a) serpophitic; (b) bastitic; (c) chrysotilic; (d) antigoritic; (e) chrysotilic-bastitic; (f) antigoritic-bastitic; (g) chrysotilic-antigoritic; (h) chrysolitic-serpophitic; (i) antigoritic-serpophitic; (j) chrysolitic-serpophitic-bastitic; (k) chrysotilic-serpophitic-antigoritic; (l) chrysotilic-antigoritic-bastitic; (m) serpophitic-antigoritic-bastitic; (n) chrysotilic-antigoritic-serpophitic-bastitic; (o) chloritic.

The serpentines have, as accessory minerals, magnetite, and other ferriferous pigments and, incidentally, chromite, picotite, pleonaste, talc, clinochlore, tremolite-actinolite, magnesite and calcite.

By their chemistry the serpentines are ortho-metamorphic rocks as a result of metamorphism from rocks of calc-alkaline chemistry of the family of the peridotites; of the serpentines analyzed some have peridotitic and the others koswitic chemistry.

The serpentinization may be supergene and hypogene, but predominantly hypogene.

I may suggest the possibility of explaining the hypogene serpentinization in the solid condition by diffusion of H^+ ions through crystalline structures, that migration happening in connection with the final activities of differentiation of the peridotitic magma. This would explain the tendency to the homogeneity of serpentines and the unchanging volume of the material that underwent the serpentinization.

I. LES SERPENTINES

DANS le district de Bragance, région NE du Portugal, affleure un massif de péridotites et de serpentines.

Dans ce massif, on trouve toutes les gammes de passage des péridotites bien conservés à les serpentines complètes. L'étude géologique et pétrographique de ces serpentines m'a permis de systématiser la classification de ces roches et d'envisager le problème de la serpentinisation.

MACROSCOPIE.—Les serpentines du district de Bragance se montrent massives, denses, en général de structure homogène, et souvent avec des cristaux de chromite.

La texture en mailles est bien visible macroscopiquement dans les serpentines les plus altérées et superficielles, rappelant la peau des ophidiens. En profondeur, les serpentines sont vert noir, homogènes, et à la surface leur couleur est variable, quoique dans la région dominent celles de couleur vert noir. En plus des serpentines de cette couleur, on en rencontre d'autres avec diverses tonalités de vert, de gris, de rouge, de rouge vineux, de jaune et diverses combinaisons de ces couleurs.

MICROSCOPIE.—Au point de vue de la texture, il est possible de distinguer divers types de serpentines.

Cependant, la texture dominante, générique à la plupart des serpentines du district de Bragance, c'est la texture en mailles. Les mailles sont limitées par des filets de chrysotile ou de serpophite. Quant à leur forme, elles peuvent être de section triangulaire, carrée, elliptique ou arrondie; elles sont de taille variable, et, parfois, on remarque que les grandes mailles se subdivisent en mailles plus petites.

Les mailles sont remplies par la serpophite, par l'antigorite, par serpophite + antigorite, ou par serpophite + antigorite + chrysotile; ces minéraux étant ou non accompagnés par la chlorite et fréquemment par la bastite.

Parfois les mailles sont de dimensions plus grandes et pleines de fibres parallèles de chrysotile.

Il est également fréquent qu'on ne trouve pas de mailles dans les serpentines et que les minéraux serpentineux se trouvent en agrégats fibro-lamellaires, rappelant le feutre.

Il existe des cas où les mailles sont en petite quantité et la roche est presque totalement formée de serpophite.

Plus rarement, dans les serpentines chloritiques, on rencontre l'arrangement sphérolitique des minéraux serpentineux (exemple: serpentine d'une traverse de la mine d'Abessêdo).

J'ai rencontré rarement l'antigorite avec une disposition fibro-radiée totale, qui conférait également une curieuse texture sphérolitique à certaines portions de serpentine (exemple: serpentine de la mine de Conlelas).

Parfois les oxydes pigmentaires, exsudés au moment de la serpentinisation, donnent, en lame mince, la couleur jaune brun à certaines portions des serpentines, avec diverses tonalités, ce qui confère, dans certains cas, une " ring-structure " nette à chacune des mailles remplies par la serpophite (exemples: quelques serpentines de Cabeço das Beatas).

Au point de vue minéralogique, c'est-à-dire en fonction du minéral ou des minéraux serpentineux prédominants, il m'a été possible de distinguer les types suivants de serpentines, qui représentent des espèces de serpentines dans une systématique naturelle:

(1) Serpentine serpophitique. Exemples: petit affleurement entre Ornovale et Bogueiro.

(2) Serpentine bastitique. Exemples: en un point de la galerie inférieure de la mine d'Abessêdo.

(3) Serpentine chrysotilique. Exemples: en divers points des travaux miniers d'Abessêdo; et en de rares points de Cabeço das Beatas.

(4) Serpentine antigoritique. Exemples: quelques serpentines de la mine de Conlelas et de 1.600 m. N. 80° W. de la Chapelle de S. Bartolomeu.

(5) Serpentine chrysotile—bastitique. Exemples: près du front de la galerie inférieure de la mine d'Abessêdo.

(6) Serpentine antigorite—bastitique. Exemples: quelques échantillons recueillis en quartre points des galeries d'Abessêdo.

(7) Serpentine chrysotile—antigoritique. Exemples: échantillons de trois points localisés dans les travaux de la mine d'Abessêdo.

(8) Serpentine chrysotile—serpophitique. Exemples: en deux points d'une traverse de la mine d'Abessêdo.

(9) Serpentine antigorite—serpophitique. Exemples: en de rares points des travaux des mines d'Abessêdo et de Cabeço das Beatas.

(10) Serpentine chrysotile—serpophite—bastitique. Exemples: quelques exemplaires recueillis dans les galeries de la mine d'Abessêdo, dans les galeries de la mine de Conlelas, à 120 m. N. NE. du point mine Abessêdo 1°, et d'un point d'une galerie de Cabeço das Beatas.

(11) Serpentine chrysotile—serpophite—antigoritique. Exemples: en divers points des galeries et des puits des mines d'Abessêdo, Terence et Cabeço das Beatas, en quelques affleurements d'Abessêdo, dans un petit affleurement entre Colado et Bogueiro, sur la rive gauche du Tuela, au NW. d'Alto do Bogueiro.

(12) Serpentine chrysotile—antigorite—bastitique. Exemples: en de rares points des galeries de la mine d'Abessêdo; et à Viscovelo.

(13) Serpentine serpophite—antigorite—bastitique. Exemples: affleurement de Zido (Vinhais), et en deux points des galeries de la mine d'Abessêdo.

(14) Serpentine chrysotile—antigorite—serpophite—bastitique. Exemples: échantillons recueillis en divers points des galeries des mines d'Abessêdo, Terence et Cabeço das Beatas; dans une éminence à environ 1.550 m. S. SW. de Carvalhais; entre Arranjada et Vale Murelo; à Regada; à 450 m. au N.W. du haut de Colado; carrière Pires Quintela (Bragance); et en quelques affleurements sur la route Portelo—Moinho dos Padres.

(15) Serpentine chloritique. Exemples: échantillons recueillis dans une traverse de la mine d'Abessêdo et en un point de la galerie de la mine de Conlelas.

Comme minéraux accessoires normaux on trouve dans les serpentines: de la magnétite et d'autres pigments ferrifères.

Comme minéraux accessoires accidentels, j'ai trouvé de la chromite, picotite, pléonaste, talc, clinochlore, trémolite—actinolite, magnésite et calcite.

Dans les serpentines, j'ai inclus les schistes antigoritiques, qui ne sont que des serpentines antigoritiques avec un aspect visible de schistosité.

De même j'ai considéré les schistes talc-antigoritiques, comme des serpentines antigoritiques talqueuses, c'est-à-dire, des serpentines antigoritiques ayant accessoirement une plus ou moins grande quantité de talc qui a remplacé partiellement l'antigorite.

Une fois notés les différents types de serpentines que j'ai considérés en fonction de leur composition minéralogique, il est facile aux pétrographes d'imaginer leur aspect microscopique. Je vais donc rapporter seulement l'aspect que présentent les minéraux dominants dans les serpentines du district de Bragance.

Chrysotile.—Il y a des serpentines dans lesquelles ce minéral est vraiment abondant et des exemples où il est le seul minéral existant. Il se montre en filets étroits généralement du type " cross-fibers," plus rarement " longitudinal-fibers." On trouve chrysotile α constitué par des fibres négatives, et du chrysotile β formé par des fibres positives. Il y a des serpentines avec des mailles rectangulaires allongées, dans lesquelles celles-ci sont remplis par des fibres de chrysotile disposées parallèlement mais perpendiculairement à l'allongement.

Antigorite.—Elle est très fréquent dans les serpentines et s'offre vulgairement comme minéral essentiel. Elle est incolore. On la trouve généralement en agrégats fibro-lamellaires. Parfois les cristaux d'antigorite s'agrègent de façon à rappeler le feutre. Les cristaux d'antigorite prennent, parfois, un curieux arrangement; ils se distribuent en amas parallèles et perpendiculaires, donnant lieu à une " knitted-structure " bien visible, en nicols croisés, comme par exemple dans la serpentine à 1.600 m. N. 80° W. de la Chapelle de S. Bartolomeu. L'association de l'antigorite avec de la bastite et du clinochlore est fréquente.

Bastite.—Elle s'offre presque incolore, très légèrement verdâtre, avec un très léger pléochroïsme.

Elle s'est formée généralement par alteration de pyroxènes. Très souvent, elle présente une structure lamellaire, avec un allongement positif et elle est biaxe négative. Fréquemment, l'arrangement paralèle des fibres est net, étant accompagné de poussières de magnétite.

Serpophite.—Elle se trouve généralement associée á l'antigorite. Dans quelques serpentines elle s'offre comme minéral essentiel. Elle est amorphe et de faible biréfringence. Elle forme des veinules ou bien elle remplit totalement les alvéoles des serpentines.

Pénine.—En général, elle est lamellaire, blanchâtre, légèrement pléochroïque. Elle se forme par altération de l'édénite des péridotites, apparaissant parfois comme des agrégats fibro-lamellaires.

Ce n'est pas un minéral que l'on rencontre dans la majorité des serpentines.

Clinochlore.—Il est plus fréquent que la pénine, mais il n'est pas non plus générique à la majorité des serpentines. Il est lamellaire, blanc, d'aspect micacé, et très souvent il s'entremèle de magnétite.

Magnétite.—Elle est exsudée en ponctuations, en petits bâtonnets ou acicules et en globules. Au coeur des veinules de chrysotile et de serpophite, on trouve souvent de la magnétite globuleuse ou formant la région centrale d'une veinule zonée.

La magnétite montre parfois une disposition filiforme, séparée par des cristaux lamellaires de clinochlore. Elle prend aussi un curieux aspect arborescent, dendroïde. La magnétite s'entremèle fréquemment d'antigorite.

Chimisme.—La serpentine de la carrière Pires Quintela, district de Bragance, présent les caractéristiques minéro-pétrographiques suivantes: formé d'antigorite, de bastite et de serpophite, accompagnées de poussières de magnétite et accessoirement de quelques cristaux de chromite. Elle offre des régions où domine la serpophite et des portions où domine l'antigorite.

Elle a en certaines portions une structure en mailles, les parois des mailles étant formées par d'étroites veinules de type " cross-fibers " de chrysotile. C'est une serpentine antigorite—serpophite—bastitique.

La serpentine de Alto da Cruz, région de Donai, Bragance, est essentiellement formée d'antigorite.

Celle-ci se montre partiellement métasomatisée par du talc. La calcite s'offre en plages allotriomorphes et offre des inclusions d'antigorite. J'ai trouvé aussi un peu de bastite. Des pigments de magnétite et quelques petits cristaux allotriomorphes de ce minéral et de chromite apparaissent aussi. C'est une serpentine antigoritique talc-carbonatée.

	1	2	
SiO_2	36·29	39·21	
Al_2O_3	0·05	0·32	
Fe_2O_3	11·60	2·80	
FeO	0·98	5·72	
MgO	36·04	19·37	
CaO	0·05	15·02	
Na_2O	0·38	0·55	
K_2O	...	0·02	Analyses
TiO_2	0·30	0·10	de J. Cotelo Neiva
P_2O_5	vest.	0·14	
Cr_2O_3	0·45	0·68	
MnO	0·06	0·08	
NiO	0·28	0·28	
CO_2	...	9·55	
$H_2O > 110°$	12·25	5·45	
$H_2O < 110°$	1·81	0·46	
	100·54	99·75	

1. Serpentine antigorite-serpophite-bastitique de la carrière Pires Quintela (Bragance).
2. Serpentine antigoritique-talc-carbonatée, de Alto da Cruz (Donai).

J'ai calculé les nombres de Niggli, lesquels sont respectivement:

1	si	al	fm	c	alk	k	mg	ti	p	qz	$\dfrac{c}{fm}$	Coupe
	56	0·5	99	0	0·5	0	0·85	0·4	0	—46	0	I

2	si	al	fm	c	alk	k	mg	ti	p	qz	$\dfrac{c}{fm}$	Coupe
	73·5	1	68	30	1	0	0·80	0·1	0·1	—30·5	0·44	IV

Le chimisme de la serpentine antigorite-serpophite-bastitique de la carrière Pires Quintela est celui du magma peridotitique.

La serpentine antigoritique talc-carbonatée de Alto da Cruz se projette dans le champ éruptif du tétraèdre *al-fm-c-alk* de Niggli sur la projection du magma koswitique au chimisme duquel il s'affilie.

II. LA SERPENTINISATION

J'ai indiqué au début que les roches péridotitiques de la région de Bragance—Vinhais présentent les gradations les plus variées de serpentinisation. Il est possible également de suivre, en certains endroits, des passages latéraux des péridotites frais à des péridotites partiellement serpentinisée et de ces dernières à des serpentines complètes. Il est possible, aussi, par l'étude de lames minces de différents aspects de serpentinisation, d'admettre la sequence des états successifs d'altération.

La serpentinisation de l'olivine débute dans les fractures des cristaux et va élargissant son action peu à peu et ainsi surgissent les aspects veinulaires de l'altération de l'olivine.

Ces veinules sont formées par des fibres de chrysotile disposées, en général, transversalement à l'orientation des veinules. Au moment de la formation du chrysotile, il y a eu exsudation de magnétite qui se présente finement granulaire dans la région centrale des veinules.

Il y a des veinules qui, dans la région centrale, présentent de la serpophite, isotropique, incolore ou légèrement jaunâtre.

Il y a aussi des veinules de serpentine qui se montrent compacts, avec des couleurs de polarisation très vives, et qui dans les marges offrent une structure fibreuse.

La serpentinisation de l'olivine débute dans les fractures principales et, ensuite, elle passe aux fractures secondaires formant un réseau de mailles polygonales qui, à mesure que la serpentinisation se développe, prennent une configuration elliptique ou circulaire. Les mailles d'olivine se serpentinisent peu à peu, et s'altèrent en fibres de chrysotile, qui se montrent entrecroisées et semblent dériver par irradiation des fibres de chrysotile des veinules ci-dessus indiquées.

Parfois les alvéoles d'olivine s'altèrent en serpophite, incolore, isotropique, transparente, sans type quelconque de structure résoluble.

D'autres fois se produit l'altération des mailles d'olivine en antigorite, de structure fibro-lamellaire. Dans quelques lames minces, il est possible d'observer conjointement antigorite, serpophite et chrysotile enveloppant des restes de cristaux d'olivine.

Au moment de la serpentinisation de l'olivine il y a exsudation de magnétite, minéral qui en général prend une forme granulaire, mais, parfois, aciculaire ou de petits batonnets abondants dans quelques mailles ou alvéoles de serpentine, prédominant surtout dans celles de nature serpophitique.

Dans des roches péridotitiques avec de l'enstatite, il est possible de rencontrer divers stades d'altération de ce minéral en bastite. Cette altération est centripète. Les fibres de bastite commencent leur formation sur les bords des cristaux d'enstatite ou de bronzite, et, peu à peu, elles substituent la pyroxène. Cette altération est accompagnée d'exsudation de magnétite, plus abondante quand il s'agit de bronzite. Dans le cas de ce minéral, il est curieux que, parfois, l'exsudation de magnétite se fait de manière à ce que cette dernière reste orientée dans le métasome bastitique et laisse bien visible la position du cristal primitif de bronzite.

Dans les péridotites où apparaît de l'édénite, on constate que l'altération que présente celle-ci est de nature chloritique. La chlorite se forme le long des plans de clivage et sur les bords des cristaux.

Il est possible de rencontrer divers stades de gradation de cristaux inaltérés d'édénite en cristaux quasi totalement altérés en chlorite.

Dans quelques serpentines on trouve des cristaux de talc et de trémolite—actinolite, mais ces minéraux sont ultérieurs à la serpentinisation, ce que l'on peut dire également au sujet de la magnésite qui apparaît parfois.

Les modifications et les altérations que la chromite a soufferte au moment de la serpentinisation, dans les serpentines et parfois dans les chromitites de la région Bragance—Vinhais, ont été: fracturation, cataclastisme et séparation, en grains, des cristaux de chromite.

Quant à l'origine des serpentines, on a présenté diverses hypothèses.

Selon quelques-uns la serpentinisation n'est qu'un aspect de l'auto-métamorphisme, dans lequel les solutions actives ont eu leur origine dans le magma ultra-basique (Hess, 1933).

Il y a des auteurs qui attribuent la serpentinisation à un métasomatisme provoqué par des solutions qui tirent leur origine dans les intrusions granitiques proches des intrusions ultra-basiques et ultérieures à celles-ci (Keep, 1929).

D'autres, pour expliquer l'occurrence de larges formations serpentineuses, non associées à des gabbros, sont portés à admettre un magma serpentinique—gel serpentinique avec des cristaux et des fragments d'olivine—formé par hydration de péridotites du type accumulatif et dont l'ascension peut s'admettre grâce à des troubles à l'époque de mouvements orogéniques (Shand, 1943).

Il y a encore ceux qui croient que la serpentinisation est purement supergénique (Lacroix, 1943) et d'autres qui admettent une origine mixte, supergène—hypogénique[*] (Benson, 1918).

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[*]W. N. BENSON se réfère à diverses hypothèses explicatives de serpentinisation, commes jusqu'à 1918, et il opte pour l'hypothèse de la serpentinisation hypogénique.

Dans la région Bragance—Vinhais on peut considérer deux aspects de serpentinisation: supergénique et hypogénique.

J'ai constaté, en divers endroits, que la serpentinisation va diminuant lentement avec la profondeur (exemple: Carrazedo). En outre, il y a des aspects typiques de processus de serpentinisation supergénique et tellement connus des mineurs de la région, comme par exemple á Carrazedo, qui après extraction du minerai chromitique, ils l'exposent à l'air pendant quelques mois afin que l'olivine se serpentinise, car, augmentant de volume par serpentinisation (augmentation qui varie de 15 pour cent à 72 pour cent), elle permet une facile désagrégation du minérai ainsi que la préparation et la concentration plus efficace de la chromite.

L'augmentation de volume, par serpentinisation supergénique, pourra même expliquer les plis à grand rayon de courbure qu'on remarque dans la zone superficielle de diverses formations serpentinisées, lesquelles je n'ai pas rencontrées en profondeur. Néanmoins, cela ne veut pas dire qu'elles ne peuvent pas prendre origine dans un processus tectonique, vu que la serpentine est un matériel plastique par excellence; il est possible que quelques-uns des plis tirent leur origine des mouvements hercyniques, car il y a des plans axiaux de ces plis qui s'orientent dans la direction NW.—SE.

La serpentinisation supergénique se fait " per descensum," les minéraux des péridotites étant en contact avec une phase acqueuse. Celle-ci forme une pellicule très fine entre les cristaux des minéraux des péridotites, émigrant jusqu'à la profondeur.

Les réactions suggérées par la serpentinisation, d'une manière générale pour tous les types, hypogénique et supergénique, et celle à laquelle Hess (1933), se réfère, sont:

$$2\ SiO_4\ Mg_2 + CO_2 + 2OH_2 \rightarrow Si_2\ O_9\ H_4\ Mg_3 + CO_3\ Mg$$
Forsterite Serpentine Magnesite

$$3\ SiO_4\ Mg_2 + SiO_2 + 4\ OH_2 \rightarrow 2\ Si_2\ O_9\ H_4\ Mg_3$$
Forsterite Serpentine

$$SiO_4\ Mg_2 + SiO_3Mg + 2\ OH_2 \rightarrow Si_2\ O_9\ H_4\ Mg_3$$
Forsterite Enstatite Serpentine

$$3\ Si_2\ O_8\ Fe\ Mg_3 + 6\ OH_2 + O \rightarrow 3\ Si_2\ O_9\ H_4\ Mg_3 + O_4\ Fe_3$$
Olivine magnesienne Serpentine Magnetite
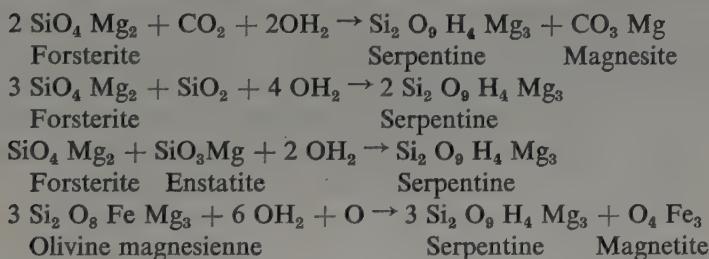
Dans le cas de la région Bragance—Vinhais—Morais, à première vue et spécialement par la présence de magnésite, la première équation est satisfaisante pour Cabeço das Beatas et Morais, mais non pour beaucoup d'autres occurrences de serpentine. Et en outre, comme je l'ai vérifié, la magnésite est ultérieure à la serpentine car elle la traverse en filons et je crois qu'elle est provoquée par altération hydrothermale produite par une différenciation du magma granitique assez ultérieure.

Hess généralise la second réaction et l'applique à tout les cas de serpentinisation et ne donne importance, attendu que ce sont des exceptions, à les deux dernières réactions.

Il est vrai que, dans la région Bragance—Vinhais—Morais, la derniére réaction doit se rapprocher de la réalité, car tous les aspects de serpentinisation supergénique que j'ai observé ont toujours été accompagnés d'exsudation de magnétite. Celle ci se montre en formations ponctuées ou en batonnets.

En outre, comme le rapport Fe_2O_3/FeO est plus grand dans les serpentines que dans les roches ultrabasiques correspondantes inaltérées, on peut admettre la présence de l'O au moment de la serpentinisation.

Je suis convaincu que cette réaction a joué un grand rôle dans la serpentinisation des roches ultrabasiques brageanciennes et se serait opérée sous l'influence de conditions supergéniques et qu'en aucun cas il ne s'agit d'autométamorphisme.

Mais la majorité des serpentines de la région Bragance—Vinhais—Morais, doit avoir une origine différente, car ce sont des minéraux d'une fort probable serpentinisation hypogénique (chrysotile β, antigorite β et bastite) qui prédominent dans ces roches, comme j'ai pu le reconnaître à divers processus.

L'existence de serpentines à une grande profondeur, comme dans les travaux d'Abessêdo, et le passage graduel et latéral de ces roches à des péridotites parfaitement conservées, portent à supposer la serpentinisation hypogénique par autométamorphisme et à nier l'existence d'un magma serpentinique.

Hess ne croit pas, d'après ses études au terrain, en un grand changement de volume au moment de la serpentinisation et il admet celle-ci comme étant de nature autométamorphique (Hess, 1933).

Et, il en est ainsi, le résidu magmatique originaire de la serpentinisation était dans les pores et les canalicules capillaires et sous-capillaires de la roche ultrabasique, et représenterait le dernier stade du cycle de l'activité ignée ultrabasique. À l'époque de la serpentinisation, par réactions de ce liquide de différenciation avec l'olivine, se seraient formés des minéraux serpentineux au lieu de pyroxènes et il y aurait eu une légère décroissance de volume. Cela aurait permit l'ouverture de fentes étroites dans les roches ultrabasiques, encore imparfaitement consolidées; elles auraient été remplies par des restes de la dite solution magmatique qui aurait donné origine à des veinules de chrysotile observables en divers endroits. L'immobilité de la solution magmatique est défendue par Hess, qui croit que cette solution contiendrait une quantité relative d'eau provenant des roches à travers lesquelles le magma ultrabasique à fait irruption.

Pour cela, il se fonde sur l'inexistence de métamorphisme de contact autour des intrusives ultrabasiques. Or c'est cela justement qui ne correspond pas à une réalité, vu que les aspects de métamorphisme de contact provoqués par les intrusions ultrabasiques sont vulgaires et intenses dans la région Bragance—Vinhais—Morais; ces aspects ont comme minéral typomorphe la grenade. Les amphibolites ou les schistes en contact avec des roches ultrabasiques présentent des grenades dans l'auréole de métamorphisme de contact.

Dans la serpentinisation hypogénique, ainsi que dans la supergénique, des minéraux anhydre se sont transformés en mineraux hydratés, dans la formation desquels intervient le radical OH. Pas conséquent, on peut dire que les réactions de serpentinisation se sont effectuées dans une phaser fluide, type de pellicule intergranulaire, et qu'il est probable que la mobilité de cette phase ait été favorisée par des déformations tectoniques orogéniques.

Quand un minéral riche en hydroxile est converté en un minéral anhydre ou vice-versa, Bugge (1946) considère comme improbable que l'ion OH^- se répande à travers la structure cristalline, mais il admet sa migration ou celle de OH_2, comme pellicule intergranulaire.

En outre il trouve inutile de supposer la diffusion de OH^- vu que l'hydratation peut s'expliquer également par diffusion des ions H^+. On a constaté expérimentalement que les ions H^+ ont un grand pouvoir de diffusion en divers silicates (Bugge, 1946).

Je crois que par un processus de diffusion à l'état solide, on peut expliquer la serpentinisation hypogenique. Les ions H^+ émigreraient à travers les structures cristallines des silicates magnésiens, et cette migration serait en connexion avec les activités finales magmatiques de " rest-magma " de différenciation du magma péridotitique. Il est possible que se soit produit la réaction suivante:

$$5\ SiO_4\,Mg_2 + 8\ H^+ = 2\ Si_2O_9H_4\,Mg_3 + SiO_2 + 4\ Mg^{2+}$$
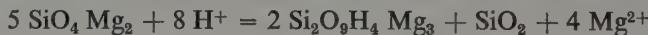
Cette réaction hypothétique s'effectuerait de telle manière que, tandis que H^+, venu du milieu externe, était introduit par diffusion, Mg^{2+} serait transporté et pourrait donner origine, dans certains cas, à des substitutions dans les régions contigües en transformant le diopside en enstatite:

$$Si_2O_6MgCa + Mg^{2+} = Si_2O_6Mg_2 + Ca^{2+}$$
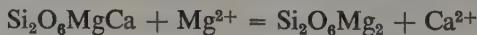
en certains lherzolites.

Il s'élève un doute sur la possibilité de la migration des ions H^+ à travers les structures cristallines sur une aire si large et si étendue. Je crois que cela est possible, quoique la migration de la matière à une grande distance à travers les structures cristallines soit encore du domaine des hypothèses de généralisation. Néanmoins, cette migration expliquerait la tendance à l'homogénéité de la serpentinisation dans son ensemble; et, en outre, cela expliquerait aussi l'immutabilité de volume du matériel qui a été serpentinisé à une grande profondeur; le problème de l'espace cesserait ainsi de nous préoccuper.

III.   CONCLUSIONS

1èr.—Les serpentines ont généralement une texture en mailles et rarement fibro-lamellaire (feutrée), serpophitique, sphérolitique et semi-sphérolitique.

2ème.—En fonction du minéral ou des minéraux serpentineux essentiels on a pu distinguer les types suivants de serpentines : (*a*) serpophitique; (*b*) bastitique; (*c*) chrysotilique; (*d*) antigoritique; (*e*) chrysotile-bastitique; (*f*) antigorite-bastitique; (*g*) chrysotile-antigoritique; (*h*) chrysotile-serpophitique; (*i*) antigorite-serpophitique; (*j*) chrysotile-serpophite-bastitique; (*k*) chrysotile-serpophite-antigoritique; (*l*) chrysotile-antigorite-bastitique; (*m*) serpophite-antigorite-bastitique; (*n*) chrysotile-antigorite-serpophite-bastitique; (*o*) chloritique.

3ème.—Comme minéraux accessoires les serpentines présentent, généralement, la magnétite et d'autres pigments ferrifères et, accidentellement, chromite, picotite, pleonaste, talc, clinochlore, trémolite-actinolite, magnésite et calcite.

4ème.—Je considère les schistes antigoritiques comme des serpentines antigoritiques et les schistes talc-antigoritiques comme des serpentines antigoritiques talqueuses.

5ème.—Par leur chimisme, les serpentines sont des formations ortho-métamorphiques, ayant résulté par métamorphisme de roches à chimisme calco-alcalin de la famille des péridotites.

6ème.—La serpentinisation peut être supergénique et hypogénique.

7ème.—Il y a des gradations de serpentinisation des péridotites frais aux serpentines complètes.

8ème.—Dans la serpentinisation supergénique la réaction $3 \ Si_2O_8FeMg_3 + 6 \ OH_2 + O \rightarrow 3 \ Si_2O_9H_4Mg_3 + O_4 \ Fe_3$ semble être la plus fréquente.

9ème.—Il est possible d'expliquer la serpentinisation hypogénique par réactions à l'état solide par diffusion des ions H^+ au travers des structures cristallines des silicates ferro-magnésiens, migration effectuée en connexion avec les activités finales de différentiation du magma péridotitique. De cette manière s'expliquerait la tendance à l'homogénéité des serpentines et l'immutabilité de volume du matériel serpentinisé. Il se passerait peut-être la reaction:

$$5 \ SiO_4 \ Mg_3 + 8 \ H^+ = 2 \ Si_2 \ O_9 \ H_4 \ Mg_3 + Si \ O_2 + 4 \ Mg^{2+}.$$

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DISCUSSION

M. K. Wells: The use of the term " serpentine " is always subject to a certain amount of ambiguity—it may apply equally to a rock type or to one of the serpentinous minerals. To avoid this confusion it is suggested that " serpentine " should be retained as a general term for the minerals, and that " *serpentinite* " should be adopted for the rock formed by them. Comparable terms such as amphibolite, pyroxenite, etc. are already in wide use for sensibly monomineralic rocks, so that the addition of the ——" ite " termination in this case would give the needed exactness without increasing an already overburdened petrographical nomenclature.

GEOCHEMISTRY OF SODIUM

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ABSTRACT

1. Old computation of age of ocean from its Na-content and the Na-delivery of rivers (Halley 1715, J. Joly 1899) leads to improbable low value of 10^8 years.

2. Balance of yield of Na by decomposition of igneous rocks against total amount of Na in sea (Clarke 1913, V. M. Goldschmidt 1937) shows that all sediments together form layer of mean thickness of 2 km. on land. A surprisingly small amount as phyllites, paragneisses and granitized sediments have to be included.

3. Much gneiss and granite are derived from shale by alkali-pneumatolysis. The addition is largely Na, said to come like magma from below.

In (1) and (2) Na is lost, in (3) it has to come from unknown source. It seems natural to suppose a circulation.

Rejection of primary, juvenile magma, i.e., of the modification to Hutton's plutonism which has become customary during the nineteenth century is compatible with geochemistry, e.g., shale-sand-limestone ratio and meets some otherwise insurpassable difficulties and gives new interest to many branches of petrological investigation.

THE most reliable data of geochemistry are those concerning the ocean. Owing to its homogeneity, its mean composition can be determined with precision. The same is true for its surface. The figure for its mean depth, 3800 m., may not be quite so accurate, none the less the values for its total mass, 140×10^{22} gr., and for the content of Na in solution, $1 \cdot 07$ per cent or $1 \cdot 5 \times 10^{22}$ gr., have mean errors which are extremely small in comparison with those of other parts of our planet.

If we try to balance this Na mass with that transported by rivers, etc., we have to content ourselves with rough estimates for the latter. Still, by their order of magnitude alone, they sometimes may lead to very disturbing or, more optimistically, very significant results.

In the beginning of the eighteenth century Halley suggested that the age of the ocean could be derived from the rate of delivery of salt by the rivers. Quantitative data were completely lacking at the time. Those available in 1899 led J. Joly to a figure of 80×10^6 years, which was then considered a probable date for the first condensation of water on the cooling earth. Nowadays it is fairly certain that this represents some time about the Upper Cretaceous. In *The Age of the Earth*, Holmes (1937) enumerates some 10 causes of errors and shows that it is eventually possible to obtain a considerably earlier date. An agreement, however, can only be reached by rejection of the principle that present conditions are representative of the past: the delivery of Na at the present time should be exceptionally high.

The total mass delivered can be considered, without bringing in time. The calculation was first made by Clarke in the second decade of this century. One of the greatest authorities on geochemistry repeated it with complete faith—V. M. Goldschmidt 1933.

$$100 \text{ gr. of mean igneous rock contain} \qquad 2 \cdot 8 \text{ gr. Na.}$$
$$100 \text{ gr. of mean sedimentary rock contain} \quad 1 \quad \text{ gr. Na.}$$
$$\overline{}$$
$$100 \text{ gr. of sediments formed deliver} \qquad 1 \cdot 8 \text{ gr. Na.}$$

total mass of sediments formed: $100 \times 1 \cdot 5 \times 10^{22}/1 \cdot 8 = 85 \times 10^{22}$ gr.

According to this result the sediments would form a layer of 2000 m. (6,000 feet) on the land-surface of the globe. Actually V. M. Goldschmidt's calculation takes into account such niceties as the difference in weight of igneous rocks and sediments. The loss of Na is overcompensated by the gain of CO_2 and H_2O, which makes the mass of sediments slightly greater than that of the

decomposed igneous rock. Less than 10 per cent are involved which, in view of the uncertainty of the Na-content of sediments, is of no consequence.

Of course, the chemically non-decomposed rocks have to be added (arkose, graywacke, tuff) but nevertheless the calculated amount of sediments is surprisingly small. It would perhaps be of the right order of magnitude if only fossiliferous strata had to be considered. The fact of their later on having been submitted to metamorphosis cannot have influenced the earlier process of weathering and sedimentation, and therefore all phyllites and mica-schists have to be included, and for that matter most of the bulk of gneiss and granite too, in so far as they are considered as derived from sediments. (The same material may have gone through the cycle sedimentation—gneissification—weathering—sedimentation more than once, which decreases the total calculated mass of sediments).

The alkali which is added to shales during their transformation into gneiss and granite is believed to be of primary magmatic origin. The recognition of widespread granitization processes, which transforms sediments into igneous-looking rocks, makes the function of the magma less clear than it was in the views of the Heidelberg school. Goldschmidt was convinced that igneous rocks are simply derived from a juvenile melt and that in metamorphism the migration of chemical elements played a very subordinate part, so much so that in connection with his estimation of the total mass of the sediments he never once mentions its possibly disturbing influence. This is the more remarkable as he has specially drawn the attention to migration in metamorphism by his study of contact phenomena in Norway, which showed that an alkali transport must have occurred over a distance of some kilometres outward around intruded batholiths. At present it is generally believed that in regional metamorphism material must have been added on a world-scale: this transport has to consist largely of Na.

The low values found for the age of the ocean and for the total mass of sediments suggest that there has been more Na brought into the sea, than there is now to be found, while in metamorphism Na comes forward from an unknown source. One is tempted to think of a circulation.

One of the items on Holmes's list of factors modifying the calculated age of the ocean is " the possibility that sodium may be returned to the sediments on the sea floor by base exchange." It is difficult to estimate its importance; it might be considerable. Would not it then be natural to suppose that this is the Na which is re-encountered in sedimentary gneiss and granite?

S. J. Shand comes to the same suggestion from the other side of the problem. " To throw all responsibility for the world-wide granitization of sediments upon a hypothetical ichor is not a satisfactory solution." He mentions " a more prosaic solution; namely the redistribution of alkalis by connate water contained in the pores of the sediments " which would lead to " the redistribution of matter that is already there, rather than the introduction of new matter." (*Eruptive Rocks*, London 1943, p. 224.)

The derivation of plutonic and even volcanic rocks from sediments, again advocated by a number of modern petrologists, leads to conceptions where magma tends to lose more and more of its primary importance. If it now has to be relieved of the Na-transport also, the question arises whether there are still functions left for juvenile magma, which are important enough to justify its existence; whether it is not possible to explain the facts of observation with nothing but sediments.

In the original plutonism of Hutton, the magma consisted of remelted sediments. It would be an interesting historical study to see how it came about that this origin has been rejected. And then to see whether the grounds for this rejection did not become spurious in the light of later acquisitions of science. We would then have to consider the data of geology, geophysics, geochemistry and petrology in their compatibility with this pan-sedimentary petrogenesis.

The whole interest which could be derived from such an investigation, depends on whether anything more definite can be postulated, than merely that every rock or lava once has been a sediment. If we suppose that sediments were molten on a large scale and thoroughly mixed, this melt could hardly be different from juvenile magma, and therefore would provide us with all the usual (lack of) explanations of magmatic theories.

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An attractive point in Hutton's theory of the earth is uniformitarianism, the belief that present-day conditions are representative of the past. It seems just as true now as in his time, that by " physical inquiry we find no vestige of a beginning."

We must not suppose that at any time there have been large cisterns filled with molten material, for geophysics show them to be absent at present; there will not have been more magma in a molten state than is needed to feed volcanoes. Here we see it rise to the surface, not with the rush to be expected when a big volume of liquid was present, but apparently at the limited rate at which it is formed in depth.

Therefore it is not likely that mixing of molten sediments took place on a large scale. The variation in composition of sediments will afford an explanation for the different types of igneous rocks. The sorting during sedimentation has to replace the differentiation of the juvenile magmatic theory. This of course, offers a ready explanation of the ortho-para convergencies of gneiss, amphibolite, etc. indeed so much so, that these would be more apt to draw attention to the pan-sedimentary viewpoint, than the geochemistry of sodium, were it not that they are such a very common thing for every petrographer.

For gneiss and granite we have to suppose that Na, adsorbed by clay, is captured in feldspars during metamorphosis, and that it escaped from non-metamorphic sediments.

For the formation of a rock of gabbroid composition from limestone or marl, escape has to be supposed of a number of elements; for this case we cannot but admit that this really can take place because of the occurrence of undoubtedly para-amphibolites. This escape of material seems to be of fairly common occurence, as can be judged from what is constantly brought to the surface by mineral springs. A striking example of escape without any sign of *qua* or *quo* is also offered by styloliths.

So much for justifying the following set of rules, which are an attempt to delineate a working basis for the pan-sedimentary principle.

(1) Uniformity, as strict as possible. (It will of course be hard to deny that at present there is less uranium than 3×10^9 years ago.)

(2) Some materials like $CaCO_3$ and other soluble salts, SiO_2, ores, move freely: " percolate." It could be explained as movement of a phase, liquid in comparison with the others, under the influence of strain.

(3) Percolating material has a tendency for being gathered together in concretions and veins or continues to flow until the surface is reached.

(4) It does not spread out homogeneously through pre-existing rocks. No homogeneous mass (on the scale on which granite may be called homogeneous) is transformed into another homogeneous mass by addition of material.

A few examples will elucidate the sense in which these rules are meant to be taken, and how they work. As there often will be occasion for a comparison with the usual primary magmatic, Heidelbergian or classical theory, the abbreviations *juv* for juvenile magmatic and *sed* for all-sedimentary will indicate which of the two is under consideration.

Let us begin with the geochemistry of sodium. (sed) During geological time, that is since the beginning of the record of rocks, the ocean has been about as salt as to-day. The rivers bring in salt (*a*) from weathered rocks, (*b*) from springs deriving it from deeper seated unmetamorphosed sediments. In the long run this is counterbalanced by (*c*) which is absorbed during sedimentation, mainly by clay. This balance is self regulating as it is (*c*) which is responsible for (*a* + *b*).

(sed) The total mass of sediments is very large, it has no relation to the total mass of the sea-salt. The concentration of salt in the sea is governed by this system; when (*a* + *b*) happens to be exceptionally large, the concentration of Na in the sea rises, and with it (*c*), and vice versa.

Sodium represents a class of its own, in this, that its mobility is generally great, but that it becomes fixed in tectosilicates when Si and Al are present. The conditions of temperature and strain must favour the occupation by Al of tetrahedral-centres between 4 O-ions. In clay-minerals this happens

only to a very limited extent. Generally at low temperature only minerals with Al^6 are formed. A certain tendency to be held in 4-co-ordination may be recognized in the formation of zeolites, and of adularia and albite in low-temperature veins.

As an example of a substance which is mobile in all circumstances, let us consider the behaviour of water. The fresh sediments contain much water; this is almost completely driven out during metamorphosis which (sed) accounts for soffioni, volcanic exhalations, etc. This results in the following distribution : plutonic rocks are poor in water, much is included in sediments, extensive independent masses are found.

A tendency towards a similar distribution is found for all mobile or volatile elements. Generally there is not much to choose between the explanations of *juv* or *sed*. (juv) They are driven out from the molten magma at pressure relief or during crystallization. (sed) They escape during metamorphosis.

Extreme cases are represented by chlorine and boron. Chlorine is practically absent from plutonic rocks. It occurs in volcanic exhalations, therefore (juv) some of it is still held in the magma. Most of it however must have escaped before the formation of the solid crust began, and the magma was under atmospheric pressure. We have to accept the idea of a primary ocean of hydrochloric acid.

Of boron the content of sediments is some 500 times higher than that of eruptive rocks. The total mass of decomposed eruptive rocks (juv) contained only 1/50 of what is present in the ocean alone:—

Eruptive rocks	Ocean	Sediments		
0·8	40	400—800	$\times$	10^{18} gr. Boron.

V. M. Goldschmidt (juv) who was the first to draw attention to this interesting distribution, is inclined to accept a primitive ocean with a high content of B as well as of Cl (or an atmosphere containing BCl_3). For the manifestations of boron in minerals (tourmaline) in connection with plutonic rocks and in volcanism it has to be derived for a large part from sediments. In the case of boron *juv* is forced to use explanations in the line of *sed*.

The explanations offered by *sed* seem the more simple for these distributions of mobile *resp.* volatile elements; the Urocean of hydrochloric acid in *juv* is rather disquieting because of the lack of uniformity. At which stage in the earth's history were enough suitable kations made available by weathering to neutralize this HCl? In Cambrian time the sea was perfectly inhabitable. Since then (juv) the two processes of escape of Cl from magma, and liberation of Na-ions by weathering seem to have been keeping pace nicely. Once an enormous atmosphere of CO_2 must have been there (juv) as a stock for the formation of carbonate with Ca from later-on decomposed igneous rocks.

A consideration of the distribution of Ca has a special interest, because as a silicate in magma it is decidedly non-volatile, whereas in the sedimentary form of $CaCO_3$ it is moveable in a high degree as is witnessed by the frequent occurrence of calcite-veins and is readily understood because of its solubility. A different distribution is thus to be expected in *juv* and *sed*; the distribution actually found is in favour of *sed*.

If the proportion of calcareous to acid sediments (juv) is derived from the average Ca-content of igneous rocks we find that 10 per cent of the sediments should be limestone, which is in contradiction to what is observed in nature, viz. 20 per cent. In *sed* it follows from the principle of mobility, that $CaCO_3$ is concentrated in unmetamorphic sediments, and enters in plutonic rocks to a limited extent.

The distribution of Ca in basic plutonic rocks becomes understandable (sed) if we suppose that aluminosilicates of Na (albite) are more readily formed than those of Ca(anorthite) if there is not enough Al present to form them both.

(sed) Pure limestone only can be converted into marble, or it escapes completely. If dolomite is present, this being less soluble lags behind: dolomitization.

(sed) Impure limestone and dolomite give rise to different types of plutonic and volcanic rocks, dependent on their different compositions. The most common will be the presence of clay with absorbed Na. The Ca which does not find enough Al to be bound as $CaSi_2Al_2O_8$ or Mg for the formation of $MgCaSi_2O_6$ will escape and gabbro or basalt is formed if temperature and strain allow this end term of metamorphism to be reached; otherwise amphibolite results, of which in some cases

the sedimentary origin can be deduced from field-evidence. A shortage of SiO_2 would give rise to the formation of olivine. If no clay, that is no Al, is present, most or all of the Ca will escape, and peridotite is formed. This is to be a rare rock as only a very small fraction of the original sediment is left. In this residual-sediment rare non-volatile elements (Cr, Pt) may become concentrated. If much clay is present, there will be hardly any escape of Ca and the bulk of the sediment goes to form the plutonic rock: we expect anorthosite to occur in big masses, without accompanying ores of rare elements.

In a lesser degree than to $CaCO_3$ mobility has to be ascribed to SiO_2 which (sed) may explain that the sedimentary column shows more sandstone than is calculated (juv) from the mean composition of igneous rocks.

About the calculation (juv) of the shale-sandstone-limestone-ratio from the average igneous rock, Kuenen (1941) remarked, that it is erroneous to take this average as representing the composition of the source-material of sediments; volcanic rocks will be more exposed and less resistant to weathering than plutonic rocks, and therefore the volcanics will have had a large share in the formation of sediments. By adding to the mean igneous rock a suitable portion of basalt, a shale–limestone ratio can be derived, which is in agreement with observation. The SiO_2 content of this source-material is, however, very near to that of shale, and therefore the calculated amount of sandstone then turns out much too small.

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ON THE PRESENTATION OF GEOCHEMICAL DATA

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ABSTRACT

For various reasons, comprehensive methods of presenting data are of great importance in geochemistry.

1. As is always the case when a complex series of facts has to be investigated, comparative methods and statistical analyses are necessary. Numerical tables and graphical representations are useful and facilitate the survey.

2. Immediately accessible to investigation are the conditions in the outer earth-shells and in particular those in the outer lithosphere. They distinctly show the influence of certain selection principles. Only a few sorts of atoms are frequent and the number of widespread minerals is small. It seems advisable to base methods of representation on this given state of affairs.

3. In spite of this the physical-chemical systems to be considered are of an extremely complex character and usually much more so than those of the experimental chemist. Frequently only the essential features of the processes can be explained with the aid of the general results of the study of equilibria between phases, and in many cases can only be obtained by setting up theoretical prototypes and graphically representing their behaviour under various conditions of temperature, pressure, etc.

As a result of such considerations, every geochemist must seriously examine the question as to which methods of presentation are the most useful. A certain uniformity seems desirable as all comparisons require an extensive material that should be prepared on uniform and scientifically sound lines.

It is desired here to call attention to the fact that in all work involving the comparison of chemical data, due attention should be paid to the results of atomic chemistry.

The resistance often met with in petrographic circles against a scientific and critical revision of analytical data probably has various causes. Beside the habit of merely taking over the analyst's figures, the fact that a choice must be made between several equally good methods of re-calculating analysis-values may have produced a tendency to use none at all. By examples of the method worked out by the present writer, it is proposed to show the advantages presented by any such system as against the uncritical use of weight-percentage values. Also it is hoped to show that certain criticisms made against the use of atomic and molecular values are unfounded. This applies to the direct comparison of analyses, to the calculation of mineral compositions and to the representation of ternary, quaternary and polynary systems in concentration diagrams. Besides other examples a discussion of the chemistry of the rocks of the Hawaiian islands will be given.

GEOCHEMISTRY investigates the distribution of chemical matter in the earth's crust and the nature of the chemical processes which take place there. In connection with the methods of presenting data the following three points must be considered:—

(1) As is always the case when a complex series of facts has to be investigated, comparative methods and statistical analyses are necessary. Numerical tables and graphical representations are useful and facilitate the survey.

(2) Immediately accessible to investigation are the conditions in the outer earth-shells and in particular those in the outer lithosphere. They distinctly show the influence of certain selection-principles. Only a few sorts of atoms are frequent and the number of widespread minerals is small. It seems advisable to base methods of representation on this given state of affairs.

(3) In spite of this the physical-chemical systems to be considered are of an extremely complex character and usually much more so than those of the experimental chemist. Frequently the essential features of the results of the study of equilibria between phases can only be obtained by setting up theoretical prototypes and graphically representing their behaviour under various conditions of temperature, pressure, etc.

As a result we conclude that every geochemist must seriously examine the question as to which methods of presentation are the most useful. A certain uniformity seems desirable as all comparisons require an extensive material that should be prepared on uniform and scientifically sound lines.

It is desired here to call attention to the fact that in all work involving the comparison of chemical data, due attention should be paid to the results of atomic chemistry. Statements on different substances given in weight percentages (or more generally in any form based on weight) are for the purposes in view based on inadmissible units. It is quite unscientific to set weight percentages of SiO_2 as given in rock analyses, against those of MgO, FeO, CaO, or possibly even the sum of the alkalis. For we know perfectly well that x grams of MgO do not correspond to x units of FeO or Na_2O or K_2O, etc. A point should be made of always using values which are connected according to some simple principle with comparable units, if possible in such a way that additions and subtractions have a meaning. To
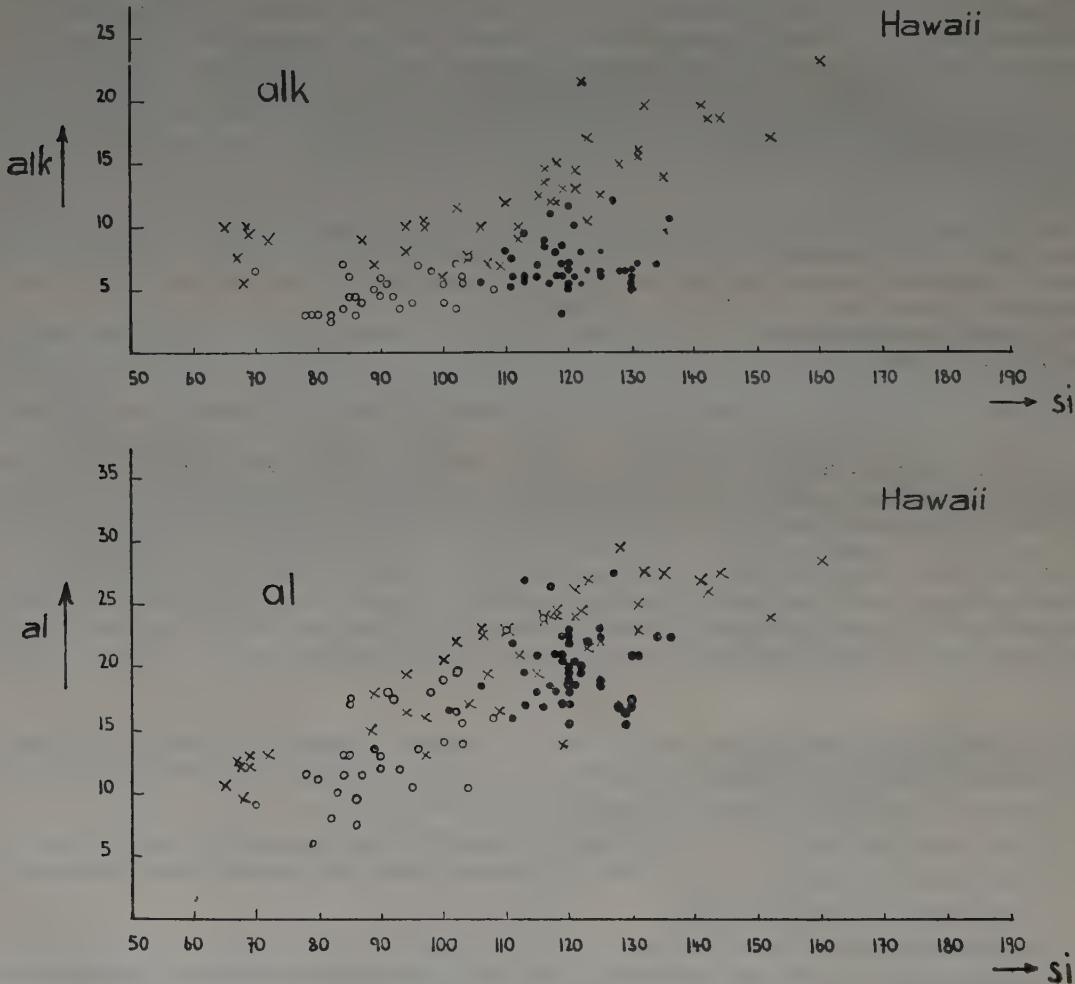
FIG. 1.—*Values of* alk *and* al *plotted against those of* si *for rocks of the Hawaiian Islands.*

combine x grams of K_2O and y grams of Na_2O to form z grams of alkali-oxides is just as meaningless as adding x grams of apples to y grams of potatoes. In dealing with things of quite different nature, additions or comparisons can only be made in regard to number of pieces, that is in our case in regard to atomic or molecular units. Weight data concerning chemically different substances must be considered as raw material which for statistical purposes requires critical revision and preparation. In the case of all chemical compounds or molecular assemblages atomic proportions or equivalents have a far greater significance and permit of more accurate deductions than numbers based on gram-units. This applies to the direct comparison of analyses, to the calculation of mineral compositions and to the representations of ternary, quaternary and polynary systems in concentration diagrams.

The resistance often met with in petrographic circles against a scientific and critical revision of analytical data probably has various causes. Beside the habit of merely taking over the analyst's figures, the fact that a choice must be made between several equally good methods of recalculating analysis-values may have produced a tendency to use none at all.

If it be desired to obtain values for the major components that are equally useful for magmatic, sedimentary and metamorphic rocks and suffer little change by the effects of incipient weathering (addition of H_2O, CO_2, O_2 out of the atmosphere and hydrosphere), it is inadvisable to use the usual
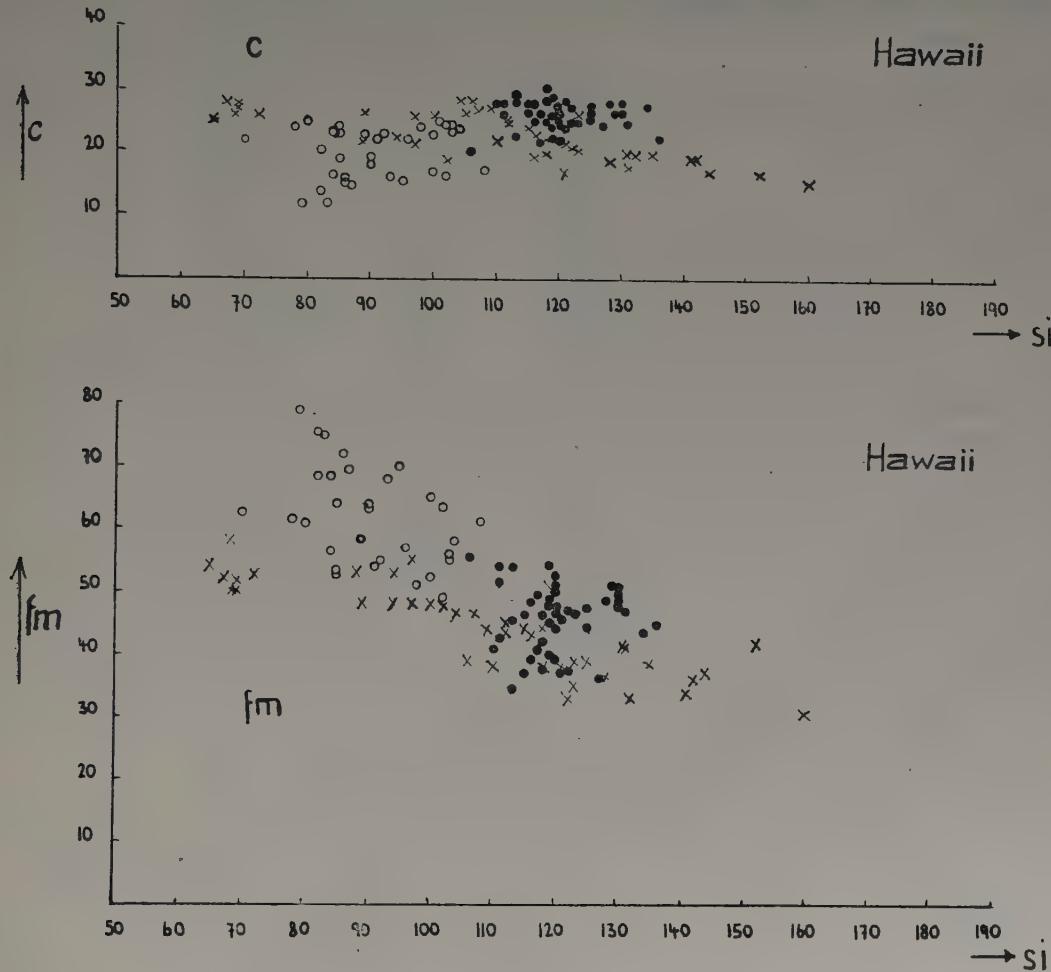
FIG. 2.—*Values of* c *and* fm *plotted against those of* si *for rocks of the Hawaiian Islands.*

atomic or molecular percentages adding up to a total of 100. A careful study of these questions led me to propose in 1920 a basis consisting of the sum of the molecular values of Al_2O_3 + FeO + MgO + CaO + Na_2O + K_2O (+ usually small amounts of the corresponding oxides Cr_2O_3, MnO, NiO, BaO, SrO, Li_2O, etc.) and always to make this sum = 100. As the state of oxidation of Fe depends on very different factors, all Fe is, to begin with, calculated as FeO. As molecular values are used, O itself is of no importance. We can equally well say that the sum of the atoms

$$\frac{Al}{2} + Fe + Mg + Ca + \frac{Na + K}{2}$$ (including the above-mentioned subsidiary components) = 100.

and thereby have the means of effecting an easy transition to sulphide or other constituents. By recalculating the molecular amounts of SiO_2, TiO_2, P_2O_5, CO_2, SO_3, H_2O, Cl, etc., or the atomic amounts

of Si, Ti, P/2, C, S, H/2, Cl, etc., in the same ratio, si-, ti-, p-, co₂-, so₃-values are obtained which can be used in conjunction with the sum = 100 of the other constituents. Silicate, carbonate, sulphate, etc. rocks can, therefore, all be treated in the same way. The rules of crystal chemistry allow the femic constituents Fe, Mg, Mn (with possible small amounts of Ni, Co, Cu, etc.) to be united, and similarly the alkaline constituents such as Na, K, Li (or Na_2O, K_2O, Li_2O) may be united as alkaline oxides. This leads to the reduced molecular values al, fm, c, alk, whose sum is 100. In conjunction with them only the si-, ti-, p- and h-values will be needed to characterize silicate rocks.

A granodiorite from Ophir Placer Co., California, with—

| si	al	fm	c	alk	ti	p
241	36	26	19	19	1·1	0·2
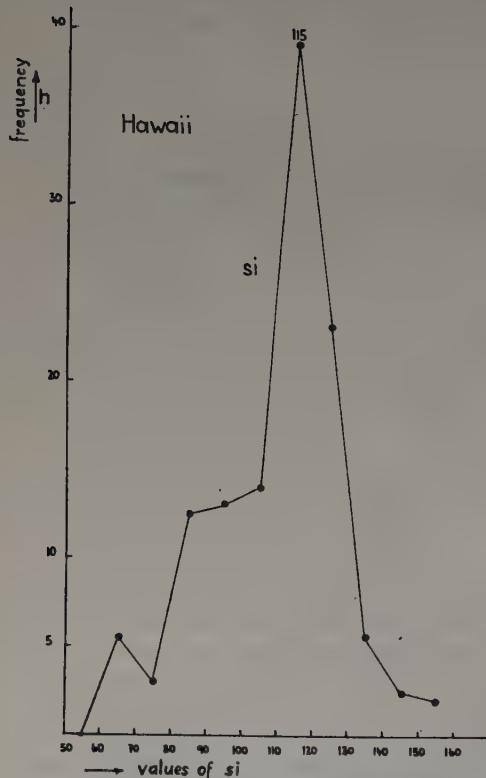
FIG. 3.—*Frequency of* si-*values found in rocks of the Hawaiian Islands.*

FIG. 4.—*Frequency of* al- *and* fm-*values found in rocks of the Hawaiian Islands.*

is, for instance, a rock in which 241 molecular parts of SiO_2, 1·1 of TiO_2 and 0·2 of P_2O_5 go with 100 molecular parts of the basic oxides. The latter contain 36 molecular parts of Al_2O_3, 26 of Fe, Mg and Mn oxides, 19 of CaO and 19 of alkaline oxides. This is a first very simple and good chemical characterization. It allows the rock to be plotted as a point within a concentration-tetrahedron, having al, fm, c and alk at its corners, and at once gives an indication of which silicate minerals can be formed. The k- and mg-values (which in the given example are 0·24 and 0·54 respectively) show in what proportions k participated in the collective component alk, and mg in the collective fm-value.

When we desire to compare a larger number of rock analyses with each other and relate them to rock analyses from all over the world, methods of comparative statistics are indispensable. Each individual analysis can first be characterized by the above mentioned small number of really fundamental values. For the volcanic rocks of the Hawaiian Isles as a petrographic unit, for example, about 130 recent rock analyses by American investigators are available. Leaving aside the relatively rare oligoclasites and trachytes, the following general characterization of the volcanic rocks of the Hawaiian Island group can be given with the above mentioned molecular values (Fig. 1-5).
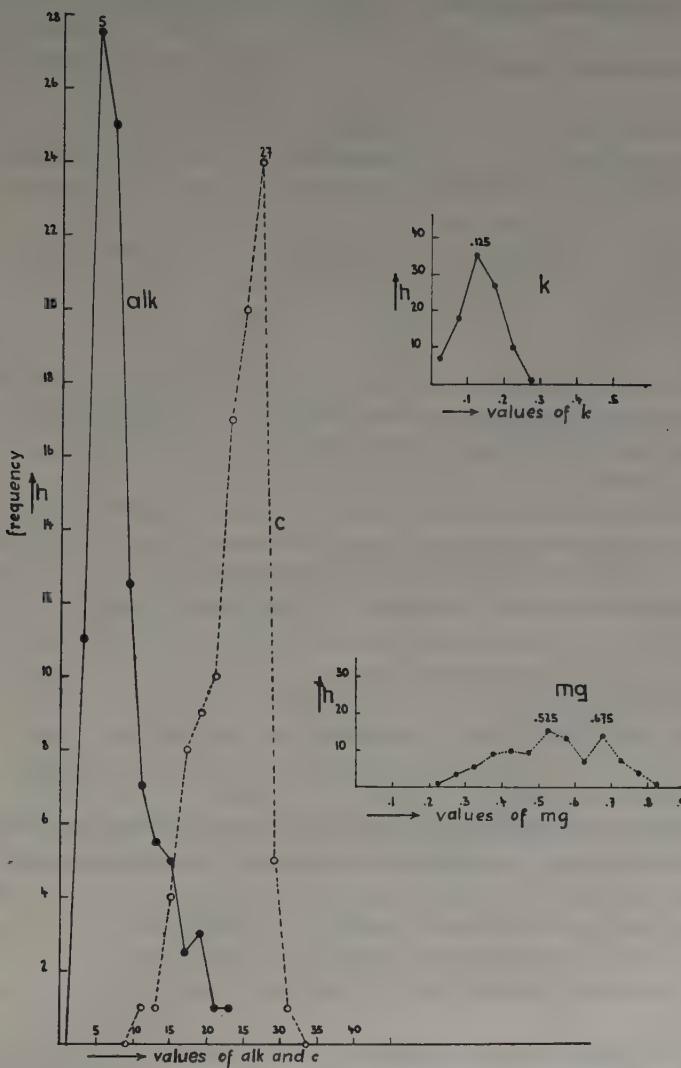

FIG. 5.—*Frequency of c-, alk-, k- and mg-values found in rocks of the Hawaiian Islands.*

si varies from about 60 to 160. The molecular proportions of SiO_2 therefore amount to between 3/5 and rather more than 3/2 of the sum of the basic oxides present. Most frequently the si values lie between 80 and 130, with a maximum frequency between 110 and 120.

fm varies between 30 and 80 and most frequently has values between 35 and 65. In about 5/8 of the analysis it lies between 40 and 55 with a maximum between 45 and 50.

al lies between 4·5 and 32 and in over one half of the instances between 15 and 25.

c shows values of between 10 and 32 and in over 5/8 of all the analyses lies between 20 and 28.

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alk is relatively low (between 2·5 and 24) and more than 5/8 of the analyses have values between 4·5 and 10.

k is low and generally below 0·25.

mg hardly sinks below 0·25 and generally lies between 0·35 and 0·7 with maximum frequencies between 0·5 and 0·55 and 0·65 and 0·7.

If we include the oligoclasites and trachytes, si can mount to 250, alk to over 40, al also to over 40, whereas fm sinks to 15 and c to below 4.

A comparison with the main variation of magmatic rocks in general brings out the following points:—

	si	al	fm	c	alk
Main variation of magmatic rocks in general (without extreme types)...	40 to about 500	0 to rather over 50	0 to 100	0 to rather over 50	0 to rather over 50
Main variation in the lavas of the Hawaiian Islands....................	60 to 100	4·5 to 32	30 to 80	10 to 32	2·5 to 24
Variation of the Hawaiian rocks including intermediate rocks	60 to 250	4·5 to 43·5	16 to 180	3·2 to 32	2·5 to 42

This furnishes a first characterization and incidentally shows that the variation in the molecular contents of the chief components of the lavas of Hawaii reflects a considerable part of the main variation of magmatic rocks in general.

In order to obtain a more detailed picture of the variation in the chemical composition, we can attempt to group the rock analyses into a small number of natural types and compare these types with types of other provinces. After these calculations no difficulty arises in making a numerical or graphical comparison between the province of the Hawaiian Islands and any other. Differences and similarity in the chemical composition will immediately become apparent. C. Burri and P. Niggli have, for instance, in their work on *The young igneous rocks of the mediterranean orogenic area* described in similar manner the alpine ophiolites, the basic rocks of Mull, of central Germany, of north Bohemia, of the Atlantic Islands, of the Bushveld, of the Marquesas Islands, the Comoren, and many other places. Further details on such comparative investigations cannot be given here. Many details are contained in the above-mentioned book.

We can summarize the method mentioned, which is now used very universally as a means of obtaining a rapid survey of the chemical composition of magmatic, metamorphic and sedimentary rocks, as follows: As comparable unit of a rock, a mass is chosen which contains in molecular form 100 parts of the mono-, di- and trivalent metallic oxides. They are combined to four groups called al, fm, c, alk after the main rock-forming oxides. The chemical formula of minerals, written in oxidic components, gives the relationship between general chemical composition of a rock and the composition of the rock minerals.

It is evident that for igneous rocks a calculation of the " norm " according to the CIPW system and a classification according to that scheme will for the purposes of comparison serve much the same purpose. But the CIPW calculation is based on weight percentages of hypothetical normative minerals and therefore often fails to bring out details which from the chemical standpoint are essential. And the task of petrographic science to work out the connections between chemical composition and mineral constituents does not apply to igneous rocks alone, but also to metamorphic rocks. Much interest is attached to heteromorphism or mineral-facies-differences, that is the possibility of rocks of the same composition possessing different mineral assemblages.

It is easy to see that for the calculation of different mineral facies the type compounds should also be given in equivalent or molecular units, just as they enter into reaction equations in the form of

chemical formulae. Then and only then can one mineral composition be easily converted into another. There are two reasons why this method was for a long time not adopted:—

(1) because the unit formulae can be chosen in any desired way,

(2) because it was not realized that by a simple choice of the unit formulae proportions can be obtained which are very close to those based on volume or weight percentages. My suggestion, made some 12 years ago, to use the so-called *molecular base* and *molecular norms* and modes-facies resulted in a very considerable simplification of the CIPW calculation and made it really adaptable without the loss of any of its advantages. I am very happy to quote in this connection some statements of Tom F. W. Barth (1948):—

"The calculation of the so-called ' norm ' [CIPW norm] is a tool which, particularly for igneous rocks, has proved its great value. But in metamorphic rocks, in which the inter-relation of mineralogy and chemistry is of the utmost importance, the norm classification has failed. The reason is obvious: The normalization of the different metamorphic mineral facies encounters great difficulties in a norm based on weight percentages. The chemical relations of a rock in terms of weight percentages obscure the comprehensive view; the computations, moreover, become unnecessarily cumbersome. I propose, therefore, that calculation of the classical weight norm be altogether discontinued. I regard it as obsolete and superseded partly by the Niggli ' molecular norm,' partly by the norm of the standard cell, as will be introduced in the present paper."

The essential principle of my calculation is as follows: All simple type-compounds or complex mineral compositions occurring in the calculations shall possess the same total number of atoms Si, Al, Fe, Mg, Mn, Ca, Na, K, Ti, P, S, etc. (that is the main cations; H, O, F, C, Cl are neglected) in the unit formula. The simplest way is to refer the equivalent weight of the compounds to a sum of these elements $= 1$ and to symbolize these unit formulae with the same abbreviations (written in capital letters) as used by CIPW.

$6\ SiO_2 . Al_2O_3 . K_2O$ containing $6\ Si + 2\ Al + 2\ K$ is therefore 10 Or.

$2\ SiO_2 . Al_2O_3 . K_2O$ containing $2\ Si + 2\ Al + 2\ K$ is therefore 6 Kp.

SiO_2 containing $1\ Si$ is therefore 1 Q.

The equation:

$2\ SiO_2 . Al_2O_3 . K_2O + 4\ SiO_2 = 6\ SiO_2 . Al_2O_3 . K_2O$ can therefore be written:

$$6\ Kp + 4\ Q = 10\ Or.$$

This approximates closely to the weight-percent relations which are as follows:

$$5 \cdot 27\ gr.\ Kp + 4 \cdot 01\ gr.\ Q = 9 \cdot 28\ gr.\ Or.$$

The atomic proportions already required for the molecular values can be used to calculate basis-compounds in which they are similarly distributed as in the CIPW calculations. Examples of such basis compounds are:

$KAlSiO_2$	$NaAlSiO_4$	$CaAl_2O_4$
3 Kp	3 Ne	3 Cal

L

Mg_2SiO_4	Fe_2SiO_4	Fe_2SiO_5	Ca_2SiO_4
3 Fo	3 Fa	3 Fs	3 Cs

M

TiO_2	$Ca_3P_2O_8$		SiO_2	
1 Ru	5 Cp		1 Q	etc.

accessories   Q

Kp + Ne + Cal is called L;   Fo + Fa + Fs + Cs is called M;   E = Q and Ru + Cp is called accessories.

The sum of the equivalent numbers brought to the sum 100 furnishes the basis in equivalent units, that is to say in comparable units of chemical compounds. As equivalent numbers are given, additions are permissible. A rock cell with the sum of 100 cations or 100 equivalent mineral compounds is called the *basis rock cell*. No auxiliary tables or recalculations are required to deduce new composition types or particular mineral compositions from the basis compounds. For example to form Ab out of x Ne, $\dfrac{2x}{3}$ Si is required. The amount of Ab formed is $\dfrac{5x}{3}$ etc. For all further details reference should be made to the original publication or to the book *Young igneous rocks of the mediterranean orogenic area* by C. Burri and P. Niggli.

Some examples will now be given to show that molecular norms calculated on these lines, very closely approach and can well be substituted for the old weight percentage norms (according to the CIPW scheme) which are much more tiresome to calculate.

So-called " andesite," Summit, Rest-House, Haleakala volcano, Hawaii—

Molecular values:

si	al	fm	c	alk	k	mg			
118	24·5	38	22·7	14·8	0·26	0·43	0·25	0·21	− 0·62

Basis:

Cp	Ru	Kp	Ne	Cal	Cs	Fo	Fa	Fs	Q
1·5	2·8	8·6	24·5	11·0	5·9	9·1	8·4	4·6	23·6

Acc. = 4·3   L = 44·1   M = 28·0   Q = 23·6

Molecular norms calculated according to Niggli:

Cp	Mt	Ru	Or	Ab	An	Ne	Cs	Fo	Fs
1·5	4·6	2·8	14·3	32·3	18·3	5·1	5·9	9·1	6·1

Molecular norms calculated according to Niggli, but on the lines of the CIPW scheme:

Cp	Mt	Ilm	Or	Ab	An	Ne	Di	Ol
1·5	4·6	5·6	14·3	26·05	18·3	8·85	15·7	5·1

Weight percentage norms according to CIPW:

Ap	Mt	Ilm	Or	Ab	An	Ne	Di	Ol
2·02	6·5	7·45	13·90	25·15	18·07	7·10	14·82	4·86

The molecular norm with its smaller content in ore corresponds rather better to the volume percentage mode than does the CIPW norm. The differences are, however, very small.

So-called " andesite," Kalahaku Cliff, Haleakala, Hawaii—

Molecular values:

si	al	fm	c	alk	k	mg			
121	26	38	21·5	14·5	0·18	0·42	0·3	0·15	−0·47

Basis values:

Cp	Ru	Kp	Ne	Cal	Cs	Fo	Fa	Fs	Q
1·7	2·4	5·8	25·7	13·5	3·6	8·8	6·5	5·9	26·1

Katamolecular norm, calculated according to Niggli:

Kp	Ru	Mt	Or	Ab	An	Ne	Cs	Fo	Fa
1·7	2·4	5·9	9·7	40·3	22·5	1·5	3·6	8·8	3·6

Kata molecular norm, calculated according to Niggli, but on the lines of the CIPW-scheme:

Cp	Mt	Ilm	Or	Ab	An	Ne	Di	Ol
1·7	5·9	4·8	9·7	37·3	22·5	3·3	9·6	5·2

10·7   69·5

Weight percentage norm according to CIPW:

Ap	Mt Hm Ilm	Or	Ab	An	Ne	Di	Ol	Biotite
2·02	14·25	9·45	34·06	25·85	3·12	6·05	5·39	—

69·36

| Vol.% 1·8 | 8·0 | | 72·48 | | — | 11·1 | 3·9 | 1·1 |

The differences between molecular norm and weight percentage norm are slight. The former agrees rather better with the volume percentage mineral composition.

Picrite basalt, Pakaoa Hill, Haleakala, Hawaii—

Molecular values:

si	al	fm	c	alk	k	mg			
78	11·5	61·5	23·8	3·2	0·14	0·7	0·56	0·2	0·09

Basis values (molecular percentages):

Cp	Ru	Kp	Ne	Cal	Cs	Fo	Fa	Fs	Q
0·5	1·7	1·4	8·5	12·5	11·5	31·1	11·5	4·4	16·8

2·2   22·5   58·5   16·8

Kata molecular norm, calculated according to Niggli:

Cp	Ru	Mt	Or	Ab	An	Wo	Hy	Fa	Fo
0·5	1·7	4·4	2·3	14·4	20·5	15·4	1·2	8·5	31·1

Kata molecular norm, according to CIPW:

Cp	Mt	Il	Or	Ab	An	Ne	Di	Ol
0·5	4·4	3·4	2·3	7·65	20·5	4·05	30·8	26·4

7·8   30·45

Weight percentage norm according to CIPW:

Ap	Mt	Il	Or	Ab	An	Ne	Di	Ol
0·67	6·03	4·56	2·22	7·34	20·57	3·12	29·93	23·88

10·59   30·13

| Mode: | 9 ore | | 25 feldspar | | | not | 39 | 25·5 olivine, |

observed   augite 1 per cent glass.

Here again the difference between the Kata molecular norm and the weight percentage norm according to CIPW is slight. But the difference between both and the modal mineral composition is considerable. The phenocrysts of augite in the picrite basalt have however been analyzed and their composition can be calculated according to the principle of the kata norm.

Kata molecular norm of the analyzed augite out of picrite basalt:

Mt	Il	An	Ne + Kp + Cal	Di	Ol
3·5	2·6	15·1	3·9	72·4	2·4

It is seen that only about 70 per cent corresponds to normative diopside and that the remainder is made up of compounds of the ore, nephelite and olivine types. It is a simple matter to add to the 30·8 per cent of Di, appearing in the kata norm, the right proportions of the other types of compound hidden in the augite. Then an alternative kata molecular norm can be calculated, in which the augite has the composition given by the analysis.

Kata molecular norm, calculated on analyzed augite:

Cp	ore	Fel	Aug	Ol	Ne
0·5	5·3	24·15	42·2	25·4	2·45

This norm corresponds very well with the modal mineral composition, though even now 2·45 per cent Ne is present, which must be contained in the glass or possibly in a rather SiO_2-poor feldspar. It must, however, be noticed that part of the normative Ne may be contained in the augite, a fact that

has often been overlooked. It is one of the principal advantages of using molecular norms that no elaborate recalculations and no tables are required for working out any desired alternative of a mineral facies.

A very clear survey of rock analyses can be obtained by plotting the basic compounds in the triangle QLM, small amounts of accessories being included in M. Apart from small displacements which result from the formation of hematite-ilmenite and magnetite, the positions of the plotted points have the following significance:
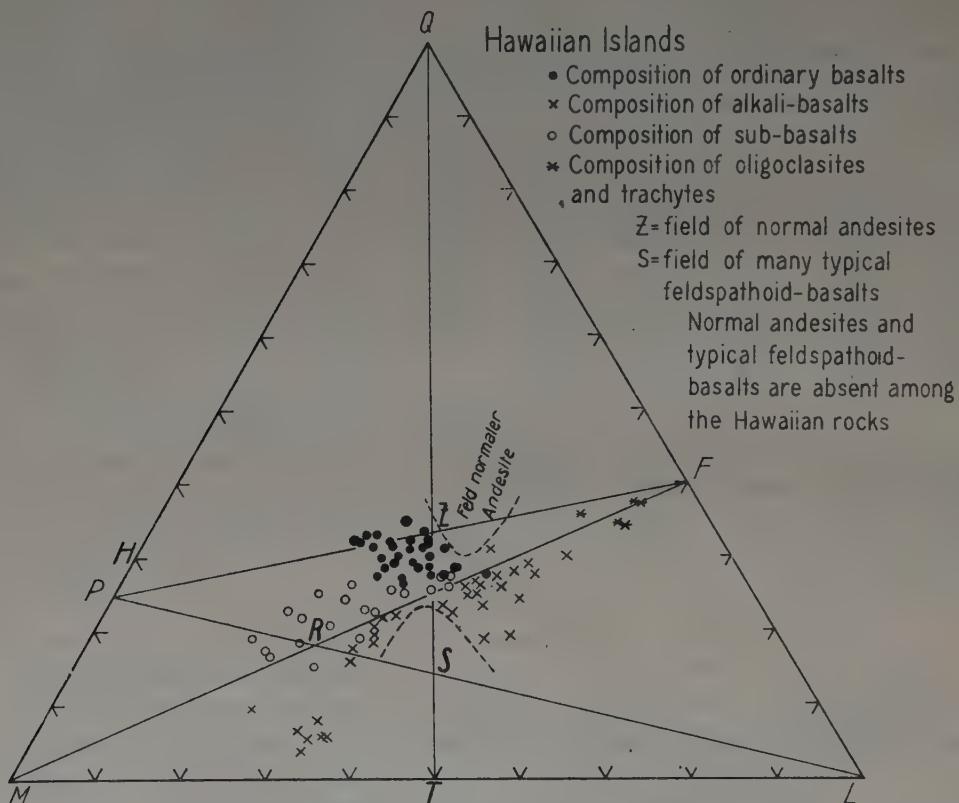
FIG. 6.—*Q-L-M-triangle for rocks of the Hawaiian Islands.*

Point within the triangle QPF: Q appears in the normal kata norm.

Point within the triangle PFM: The calculation of the norm can be carried out with the aid of compounds of the olivine-type, but without such of the nepheline type.

Point within the triangle PFL: The calculation can be so arranged that molecules of the nepheline type (including $CaAl_2O_4$) appear beside such of the pyroxene and feldspar type.

Point within the triangle FML: The lack of SiO_2 is so great that compounds of both the nepheline and olivine types are bound to appear.

If we plot the compositions of any other ideal compounds (for example of the leucite-analcite type) or of actual minerals (for example of augite from Haleakala, or the range of the melilites), we find very clear graphical connections between the chemistry of the rocks and their mineral composition. Apart from a few exceptions the points representing typical igneous rocks lie in the field HMLG

of the Figure 7, while QHG contains practically no such points. It will be observed that the published analyses of the Hawaiian Islands spread over about a quarter of the field in question in spite of being closely related to each other.

As we have seen, the molecular norm or modal mineral facies of a silicate rock differs but slightly from a weight norm or mode and but slightly also from a mode in volume percentages. This arises from the fact that all our equivalent units of compounds have nearly the same equivalent molecular weight (about 55) and nearly the same equivalent volume (about 20) as seen in Table I. The number of oxygen atoms belonging to 100 cations in a " basis rock cell " is often in the neighbourhood of 156 but varies for important minerals in silicate rocks from 133 to 200.
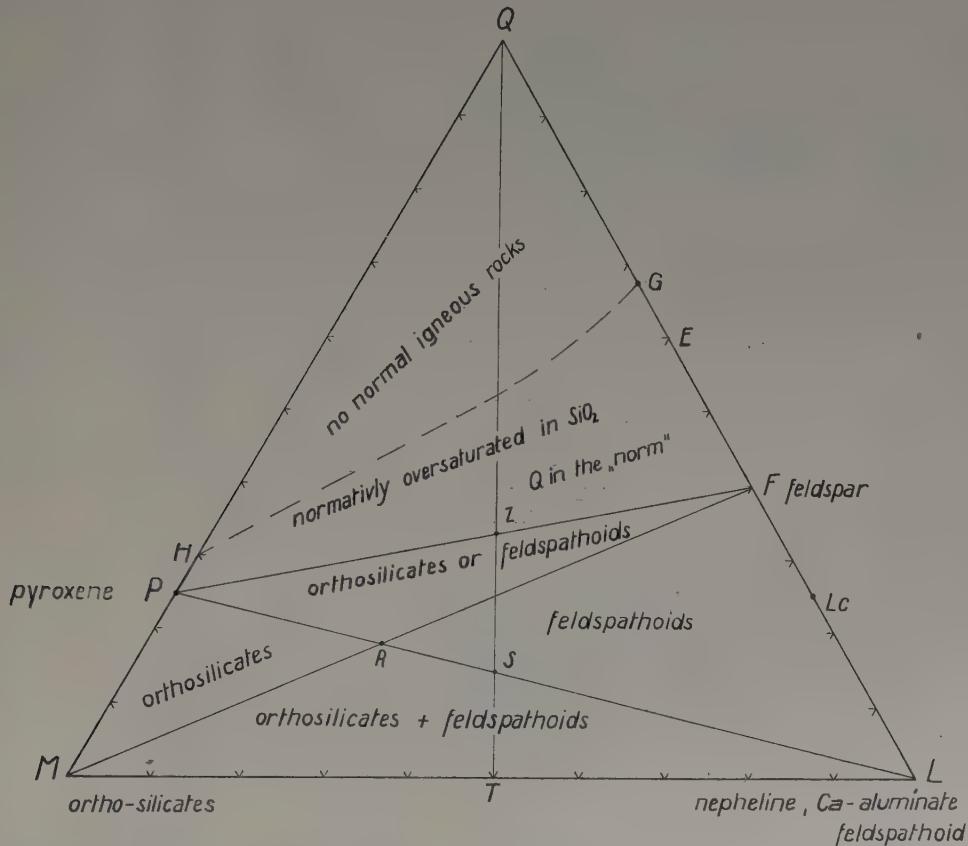
FIG. 7.—*Diagram showing the minerals normally associated with various fields in the Q-L-M-triangle for igneous rocks.*

Tom F. W. Barth has called a rock unit containing exactly 160 oxygen ions the *standard cell*. In such a cell the number of equivalent compounds (or cations) is nearly (but not strictly) 100. We know that in many rocks oxygen-ions make up about 90 per cent by volume, consequently the number of oxygen-ions is of importance for the volume relations in rocks. If the packing of the oxygen-ions were the same in all mineral structures, all standard cells should have the same volume. An analysis of the crystal structure however shows that the packing of these ions in rock minerals has a variability comparable to the variability of the equivalent volume of the compounds. If we divide the volume of the structure cell by the number of oxygens, we obtain a value approximating to the volume

occupied by one oxygen. It is for feldspars about 22×10^{-24}. Instead of 22 we have in minerals like nosean 26, in rutile 14·5 and in many dark minerals 18-16 (see Table I). The value should be constant if all standard cells have the same volume.

There are very few cases in which the variability of the equivalent volumes of the units of a basis

TABLE 1. *Important rock-minerals*
with equivalent weight, eq. volume, number of oxygens per 100 eq. units, volume of one O in the structure.

	Eq. weight	Eq. vol.	Number of oxygens per 100 eq. units	Volume for one O
Quartz	60	22·7	200	18·6
Feldspars	52–56	20–22	160	21·8–23
Leucite, Analcite, Cancrinite, K–Neph.	52–55	20–25	133–175	22·9–24·2
Na–Neph., Nosean	~47·3	18–20·6	133–150	22·5–26·2
Gehlenite-Melilite	54–60	18–19	140	~21·3
Mica, Talc, Mg-Chlorite, Serp..................	52–60	18–21·5	133–180	~18–20
Wollastonite, Zoisite, Epidote	53–58	18–20	150–162	20–22
Hornblendes............................	~52–60	17–19	150–160	18–20
Augites, Pyroxenes	~50–68	15–18·5	150	~17·5–18·5
Olivine	46·9–67·9	14·6–16·5	133	18–21·5
„ (average)........................	50–60	15–16·5		
Cyanite..............................		15		15
Sillimanite...........................	54	16·1–16·7	167	16·1
Andalusite...........................		17·1		17·1
Garnets (normal)........................	50·4–63·5	14·3–17	150	15·5–18
Cordierite (normal)......................	53·2–58	~18	162	21–22
Vesuvianite	~57	~19	~150	~18·4
Staurolite	56·5	~15	~160	21–22
Titanite..............................	65·2	~19	167	18·3
Rutile................................	79·9	18–19	200	14·5
Hematite, Magnetite	79·8–77·2	~15	150–133	~16
Corundum	51	12·9	150	16·9
Standard value espec. for leucocratic minerals	55	20	156	22
In other minerals often	50 to 80	14 to 19	variable	often 14–21

cell is much larger than the variability of the oxygen volume in different crystal compounds. In other words: it makes no great difference whether we use the basis rock cell or the standard rock cell as cells of approximately the same volume. I do not think, therefore, that the calculation of a standard

cell is really necessary for the study of replacement processes not involving marked changes of volume. But in some cases this calculation may be useful. In general, the basis rock cell with the sum of all compounds = 100 gives nearly the same insight and from Table I we always can see what kind of corrections must be considered.

Generally speaking it seems to me a question of minor importance whether the molecular units are calculated for a basis or a standard rock cell. But it is very much to be hoped that in future,

Marquesas Islands (Pacific Ocean)

- • Basalts in general
- △ Trachytes from Nukahiva and Huahuka
- × Phonolites from Ua Pou
- ✦ Titaniferous augites out of basalt from Hiva Oa

The numbers given with each point are the si-values of the basic rocks.
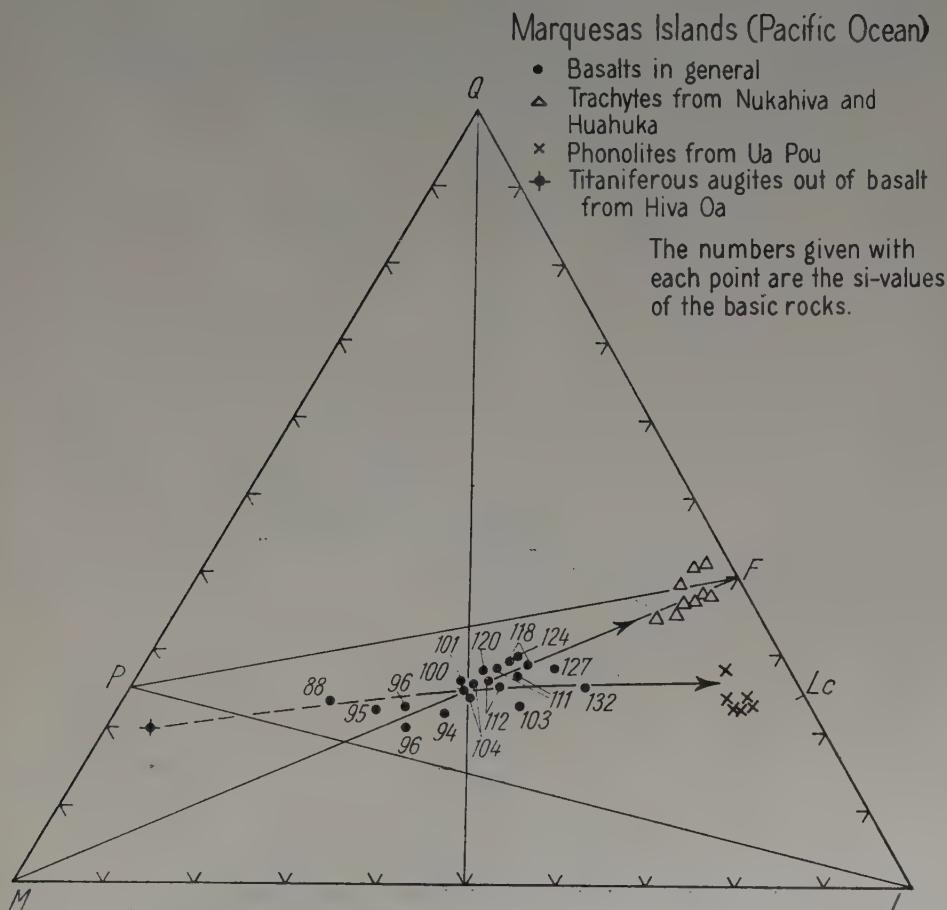
FIG. 8.—*Position in Q-L-M-triangle of rocks from the Marquesas Islands (Pacific Ocean).*

Tom F. W. Barth's statement (1948): " It is a great simplification to use molecular and atomic units rather than weight units; therefore, the weight percentages should never be taken as basis for petrographic calculations" will be generally adopted. And I conclude with another statement of Barth's, slightly modified by myself: by directly comparing the basis or standard cells of rocks under investigation one obtains a rapid review of addition and subtraction of material caused by petrogenetic processes (see for example Figs. 8 and 9).

In this way magmatic differentiation, the comparison of magmatic, sedimentary and metamorphic provinces, metasomatic metamorphism, heteromorphism and normal metamorphism of different facies can be studied more effectively than by any other method of petrographic calculation.

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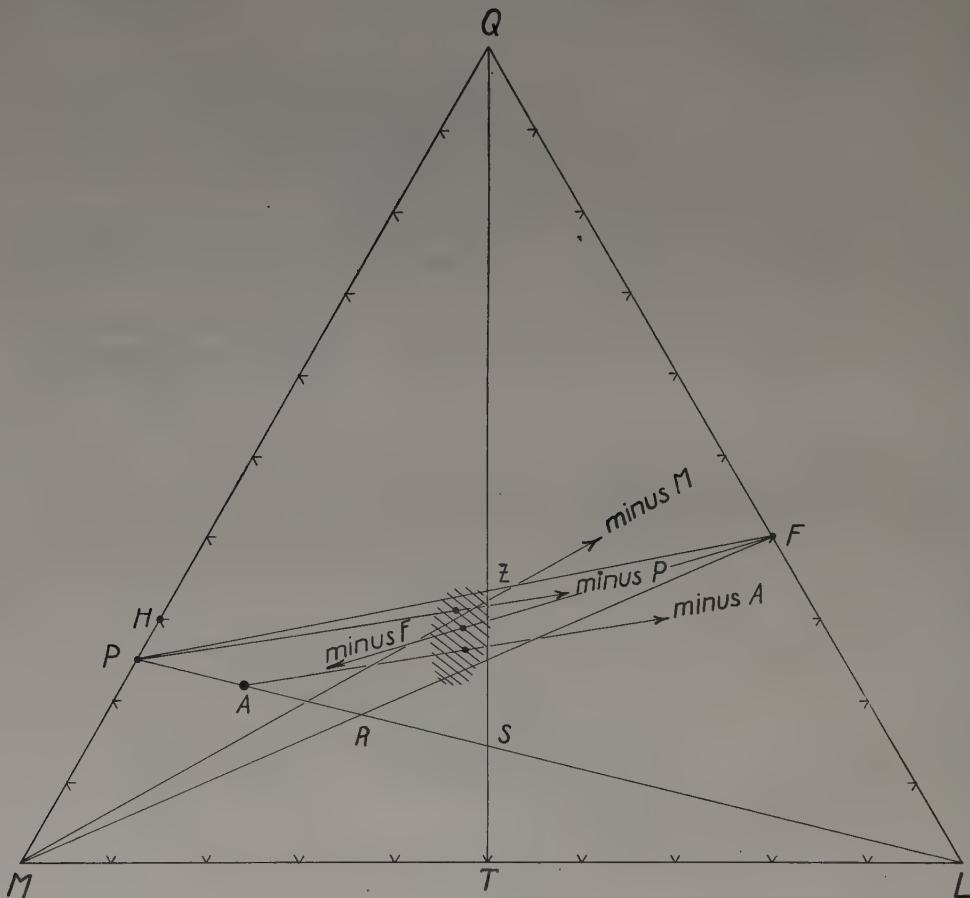
FIG. 9.—*Diagram showing relationships in the Q-L-M-triangle.*

A magma whose composition falls in the stippled area, will by the crystallisation of M (olivine, etc.), P (pyroxene, normal), A (augite), or F (feldspar) suffer a change in composition indicated by the respective arrows.

DISCUSSION

G. W. TYRRELL : At first Professor Niggli based his diagrams illustrating compositional variations in rocks on molecular values of the constituents. Later, he used in addition, quasi-mineral values in triangular diagrams. The second method is, in my opinion, the better for studying chemical variation in rocks. I prefer systems that use the values closest to mineralogical actuality; the C.I.P.W. norm, for example, is often close to the actual mineral composition, but Niggli's molecular figures are remote therefrom. The objection to using the C.I.P.W. norms in diagrams and discussions is that the variables are too many and too complex. I therefore prefer the von Wolff system (or, better, a modification thereof I have devised) in which the number of quasi-mineral units is reduced by certain groupings and becomes more amenable to treatment in triangular diagrams.

Professor Niggli used the term " normal basalt "; and, yesterday, Professor Eskola used the term " ideal granite." I wish to enter an objection to both terms on semantic grounds. There are no such rocks as normal basalt and ideal granite; they have no existence save in the minds of petrologists. The terms granite and basalt cover wide but definable fields, but ideal granite and normal basalt find no place therein. Petrological discussion would gain in clarity if such terms were avoided.

S. J. SHAND: The computation of the " norm " led to a great advance in the correlation of petrographic with chemical data. Professor Niggli has made a further advance by employing molecular proportions rather than simple percentages of the oxides. But both methods of computation are worthless unless the chemical analyses upon which they are based have a high degree of accuracy, and this unfortunately is not always the case. To the speaker it seems desirable to study and compare rocks in terms of the actual mineral composition or mode rather than any kind of norm. It is possible to determine the mode of a rock with considerable accuracy by means of the microscope, supplemented by the micrometer, the electromagnet and by heavy liquids. The function of chemical analysis is to supplement these methods but not to replace them.

P. NIGGLI (in reply): We have to use the simple molecular values *and* the basis compounds because the latter are formed with the use of some rules which do not always correspond with nature.

The chemical composition is a fundamental factor in studying the rocks, Professor Grout and Professor Larsen have shown what care we have to take in analysing rocks.

SPECIAL FEATURES OF THE OSLO IGNEOUS FELDSPARS

By C. OFTEDAHL

Norway

ABSTRACT

The feldspars of the main types of igneous rocks of the Oslo Region have been investigated, chiefly by the Universal stage. Various facts were found, that alter many of the statements of the partly antiquated descriptions of Professor W. C. Brögger—statements which are cited in many recent textbooks on mineralogy and petrography.

The plagioclases form important constituents of some important rocks: rhomb-porphyries, larvikites, lardalites, partly nordmarkite, and related rocks. The plagioclases were not correctly determined, because they have albite twins with lamellae which are so thin that they only can be seen in sections approximately vertical to (010). In other sections the plagioclases seem to be (pseudo-) monoclinic alkali feldspars.

The alkali feldspars are transitional from cryptoperthites to microperthites. The cryptoperthites belong to the " orthoclase-microperthite series " of Ed. Spencer, established on pegmatite feldspars. Various facts concerning the optics of these cryptoperthites are given.

INTRODUCTION

THE papers published by W. C. Brögger during the years 1890-1900 made the Oslo region well-known as a petrographic province of considerable interest. Some later publications are characterized by the petrographic methods of that period. During the later years petrographic investigations of the Oslo rocks have been taken up again, and when the present author began a study of the plutonic rocks, he soon found out that it was necessary to undertake a special investigation of the feldspars, because the feldspars showed some special features, which made the partly erroneous determinations of Brögger understandable. These features are the following:

(1) The acid plagioclases are twinned according to the albite law, with lamellae which often are so thin that they are seen only in special sections. In other sections they seem to be monoclinic, with some optical data similar to those of the alkali feldspars.

(2) The alkali feldspars belong to a series orthoclase-cryptoperthite. This series has been described by Spencer (1937) from pegmatite feldspars, and the Oslo feldspars show corresponding optical properties.

According to the ordinary textbooks of mineralogy the mentioned features seem to be special for the feldspars of the igneous rocks of the Oslo region, but this certainly is not correct. It is possible that these features are common in alkaline igneous rocks.

In the following the pseudomonoclinic plagioclases and the orthoclase-cryptoperthite series are described briefly; then some remarks on the high temperature feldspar problem are presented.

THE PSEUDOMONOCLINIC PLAGIOCLASES

The rhomb-porphyry is one of the most conspicuous rock types of the Oslo region. The composition of its rhomb-shaped feldspar phenocrysts have been much debated, especially around 1880 (for references, see Oftedahl (1946, pp. 50-51)). Brögger thought that the feldspar was a soda-microcline, later called anorthoclase, and this assumption was believed, and is now to be found in every textbook on mineralogy.

In 1943 the author began a study of the rhomb-porphyries and associated rocks. It was easy to determine the composition of the rectangular phenocrysts of the so-called rectangle porphyries on the Universal stage, because they are twinned with broad twin lamellae. Then it was soon found that even the apparently non-twinned rhomb-shaped crystals were twinned according to the albite law, but the

twin lamellae are usually so thin that a crystal must have the zone (010) parallel to the slide, if the twinning is to be seen by the ordinary polarizing microscope. Therefore Brögger and co-workers very seldom saw any twinning, and they believed that the feldspar was some type of alkali feldspar. In sections nearly parallel to (001) this feldspar seems to be monoclinic, because mostly the two sets of lamellae balance each other. In sections parallel to (010) the feldspar has an extinction angle, which rapidly changes with the composition.

The rhombic outline of the crystals, determined by the faces ($\bar{2}$01), ($\bar{1}$01), and (110), is obviously connected with this special type of albite twinning. Thus the phenocrysts of the rectangle porphyries are rectangle-shaped and have broad lamellae (composition 45-40 An), but the lamellae seem to disappear, when the rhomb-forming faces develop, at about 40 An. Just the same relation is found in the plutonic rocks, which are often semi-porphyric.

The monzodioritic rock type kjelsåsite is slightly more basic than the monzonitic larvikite. The large rectangular feldspar individuals of the kjelsåsite are andesines, and their albite twinning is seen in every slide. The often rhomb-shaped feldspar crystals of the larvikites are oligoclases, and in few slides twinning is seen. In transitional types with a plagioclase composition about 30 An, the plagioclase has very thin twin lamellae, but these are usually seen in the slides. The faces of the plagioclase crystals are both the rhomb-forming (110), ($\bar{2}$01), and the rectangle-forming (001), (010), ($\bar{1}$01). It is interesting to note that the change in crystal habit, followed by the occurrence of the nearly submicroscopical twinning, occurs at a composition of 40 An in the effusives, and at 30 An in the plutonic rocks.

The sub-microscopical albite twinning (a characterizing, but not quite correct expression) is also present in the large feldspar individuals of the lardalite and in some varieties of nordmarkite, mostly called pulaskite by Brögger.

The new interpretation of the feldspar in the mentioned rocks causes a change in the systematic position of these rocks. Thus the larvikite is no longer an augite syenite, but an augite monzonite, and the lardalite is not a nepheline syenite, but a nepheline monzonite. In a similar way the basic varieties of nordmarkite are no true nordmarkites (alkali-syenites), but ordinary syenites, with alkali feldspar, some oligoclase and ordinary amphibole.

The optics of the aggregate crystals consisting of sub-microscopical albite lamellae differs from that of the plagioclase of the lamellae. On account of the symmetry of the albite twinning, the aggregates get a monoclinic symmetry, if the two sets of lamellae optically balance each other. The measurements on the Universal stage show that the aggregate crystals are usually monoclinic, or nearly so (deviation of 1-3°). Then the only means of characterizing such crystals is the extinction angle a: α on (010). This angle is very similar to that of the corresponding ordinary plagioclase, because the plagioclases in question have a composition ranging from 15 to 30 An, and the plagioclases of this interval have their α very near to (010). Most certain, however, the composition is determined on powder by immersion liquids. Also then α is equal to α of the ordinary plagioclases, so that the usual tables may be used.

The sub-microscopical albite twinning does not only occur in the plagioclase phase of the Oslo rocks, but probably also, at least to some extent, in the alkali feldspar phase.

The alkali feldspars are either cryptoperthites or microperthites. The former feldspar consists of submicroscopical lamellae of orthoclase and albite, and Weissenberg photographs show that even this albite is twinned on (010)—no doubt an albite twinning.

THE ALKALI FELDSPARS

The alkali feldspars are abundant in the following rocks: kjelsåsite, larvikite, lardalite, nordmarkite, ekerite, granite, and pegmatite. In the three former rock types the feldspar is mostly clear and homogeneous. The nordmarkite has transitions from homogeneous to microperthitic alkali feldspars; the ekerite contains a typical microperthite while the granite carries a turbid orthoclase.

In all rocks but the granite the original feldspar is believed to be homogeneous, the perthitization

being late magmatic or magmatic hydrothermal. This homogeneous feldspar has been investigated in all the mentioned rocks, and it proves to be a cryptoperthite, and it forms an interesting series, the orthoclase-cryptoperthite series.

By the Universal stage the only property to be measured is the extinction angle a:α on (010). In nordmarkite an angle of 12-14° is found, and in the syenite pegmatites the angle is mostly 12°, in accordance with Brögger (1890, p. 533). The extinction angles in kjelsåsite and larvikite vary considerably, from 6° to 14°, mostly 8° to 10°.

The index of refraction may be measured on powder, but the index varies with the three components Or, Ab, and An, entering into the cryptoperthites, and therefore the index gives no easy way of classifying these feldspars.

The chemical composition is shown by Fig. 1. The cryptoperthites of the nordmarkite and the syenite pegmatite are known from analyses of the pure feldspars, while the cryptoperthites of larvikite and kjelsåsite have compositions, calculated from analyses of the rocks or of the total feldspars.
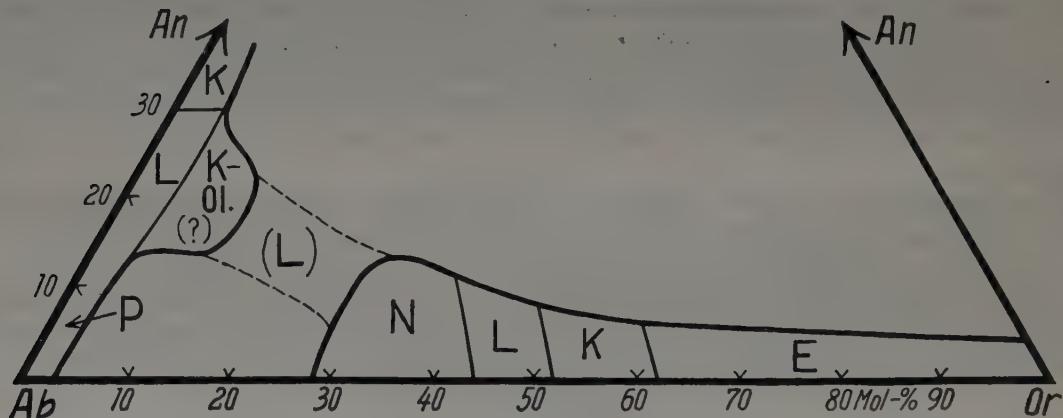
FIG. 1.—*The chemical composition of the plagioclase and alkali feldspar phases of the important plutonic rocks of the Oslo region.*

E: Oslo essexite, K: Kjelsåsite, L: Larvikite, N: Nordmarkite, lardalite, and pegmatite. E and P: Feldspar phases of the cryptoperthites. K–01: Possible field of a potash oligoclase.

The measured properties of the cryptoperthites show that they belong to the series which was called the orthoclase-microperthite-series by Spencer (1937). But Spencer's microperthites were treated as if they were homogeneous feldspars, because they are nearly sub-microscopical. The author prefers to call such feldspars cryptoperthites.

The data obtained from the Oslo cryptoperthites are too scanty to give definite general informations on this interesting feldspar series, but by using the tables of the later literature, where both composition and all optical properties are given, it is possible to draw some tentative diagrams for the variation of the optical properties with the chemical composition within the orthoclase-cryptoperthite series.

The variation of the index of refraction with the composition is shown by Fig. 2. This diagram seems to prove that the mean index of refraction varies rectilinearly within the ternary feldspar diagram, or nearly so. Some feldspars which may be true sanidines are also plotted, but the error is not serious, because Spencer (1937, p. 472) has shown that a cryptoperthite which is homogeneized, changes its mean index about 0·002 or less.

The extinction angle a : α is also greatly influenced by the An content of the cryptoperthites, so the variation of this property also must be drawn in the ternary Or-Ab-An diagram. Most authors have thought that the curves for equal extinction angles are straight lines, as shown by Fig. 3a. But the author considers, from the collected data, that the curves run as shown by Fig. 3b.
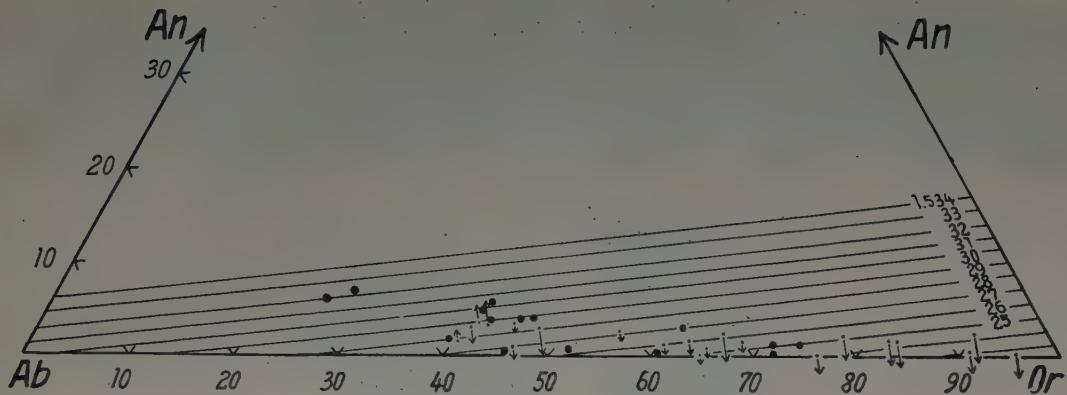
FIG. 2.—*The mean index of refraction* $\dfrac{\alpha + \gamma}{2}$ *of the cryptoperthites in relation to their composition.*

The equi-fractional curves are drawn straight-lined, determined by the mean index of adularia and acid plagioclases. The small points indicate the composition of the plotted cryptoperthites in the Or-Ab-An system. The heads of the corresponding arrows mark the mean index of refraction. Thus the length of the arrows indicates the difference in refraction between what is measured and what should be expected if the equi-fractional curves were correctly drawn. When this difference is less than 0·0005 a filled ring is used. Data of feldspars from outside the Oslo region from: Spencer (1937, Table 18); Larsen: *Amer. Mineral.*, vol. xxiii, 1938, p. 421; Wolf: *Bull. Geol. Soc. Amer.*, vol. xlix, 1938, p. 1618; Seto: *Jour. Geol. Soc. Tokyo*, vol. xxix, 1922, p. 316.
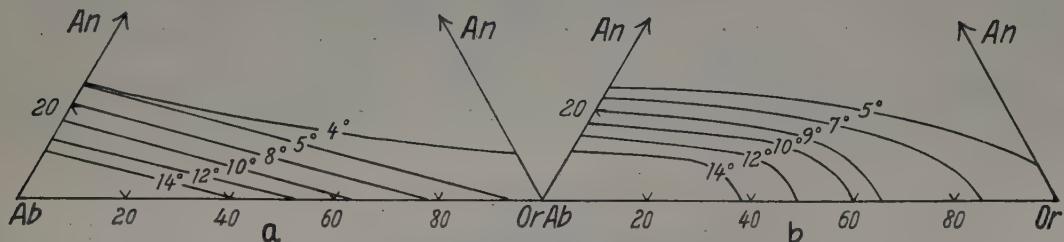
FIG. 3.—*(a) and (b). Possible diagrams showing the relation between the extinction angles on (010) of cryptoperthites and their chemical composition.*
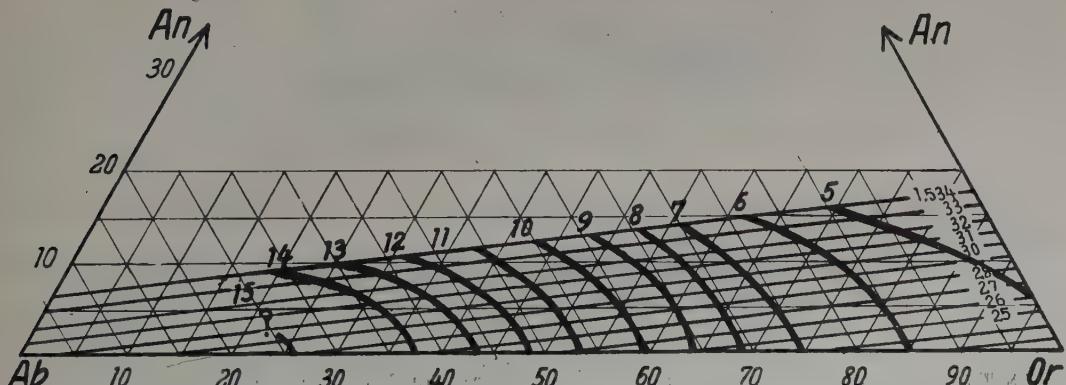
FIG. 4.—*Tentative diagram for determination of the composition of cryptoperthites by the mean index of refraction and the extinction angle on (010).*

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By combining the diagrams of Fig. 2 and Fig. 3b a diagram is established, which permits a determination of the composition from the extinction angle and the mean index of refraction (Fig. 4).

The symmetry relations of the Oslo cryptoperthites are shown by Fig. 5. Theoretically an aggregate crystal, consisting of lamellae of monoclinic orthoclase and pseudo-monoclinic plagioclase, should have monoclinic symmetry. The deviations must chiefly be explained by the fact that the pair of lamellae are not always equal in total thickness.
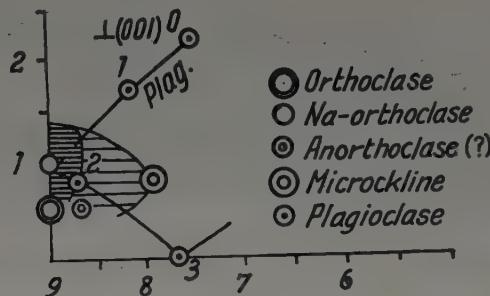
FIG. 5.—*Central part of the octant stereogram of Table 7 from Nikitin (Die Fedorow-Methode, Berlin, 1936), a stereogram vertical to β.*

Only the poles of (001) are plotted. The heavy stippled area marks the variation of the pseudo-monoclinic crypto-perthites, while the faintly stippled area illustrates the orientation of definitely triclinic cryptoperthites.

The axial angles of the Oslo cryptoperthites vary greatly, even within the individuals of one slide. Angles (—)2V between 55° and 94° have been measured. The interval 70-80° is the most usual. It is evident that the axial angle is more dependent on the cooling history than the composition. Therefore it is also useful for establishing the different alkali feldspar series.

The different series of the system Or-Ab are still uncertain, but the author thinks that a new stability diagram may be drawn, based on the published data of the last decennium. The series of Fig. 6 are:
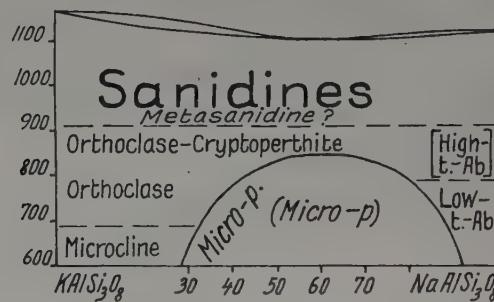

FIG. 6.—*Stability diagram for the system* $KAlSi_3O_8 - NaAlSi_3O_8$.

1. The sanidines, a possibly continuous series Or-Ab. It has low axial angles and an extinction angle constantly about 5°.

2. The orthoclase-cryptoperthite series, a discontinuous series of intermediate temperature. It has high axial angles and high extinction angles, increasing with the soda content.

3. The above series fade into the orthoclase-microperthite series, with the microcline-micro-perthite series as the most low temperature member, characteristic for the metamorphic rocks.

The name metasanidine is suggested for a group of feldspars which are sanidine-like, but have high extinction angles and low axial angles. These feldspars must be sanidines with a partial ex-solution to cryptoperthite. They seem to be frequent.

THE HIGH TEMPERATURE PLAGIOCLASES

Plagioclases of effusives are known to have an orientation of indicatrix slightly different from that of plagioclases in plutonic rocks (for references, see Oftedahl, 1945, p. 78). The problem is then whether there is an even transition between these series, or if they represent different modifications. Measurements of 11 Carlsbad twins from basalts and rectangle porphyries of the Oslo region seem to indicate a transition.
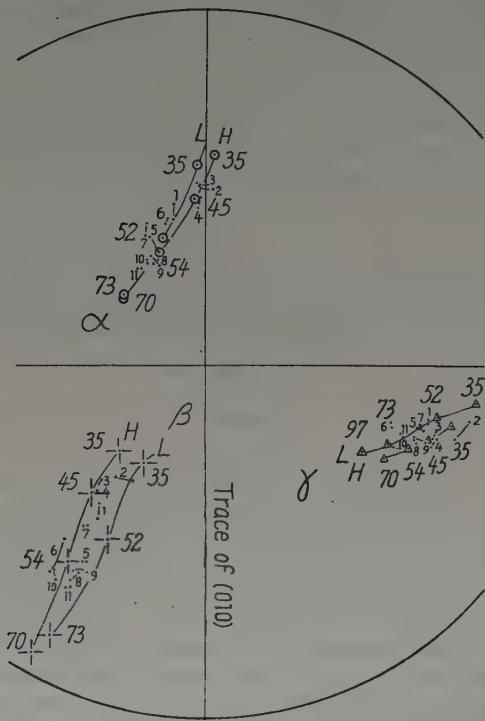

FIG. 7.—*Stereogram vertical to the c-axis.*

The migration curves for the low temperature optics (L) are taken from Duparc and Reinhard: *Mem. Soc. Phys. Geneve,* vol. xl, 1924, Pl. 11. The corresponding H curves are given by Tertsch: *Min. Petr. Mitt.,* vol. liv, 1942, p. 203. The numbers indicate the points for α, β, and γ viz. of the 11 measured Carlsbad twins.

Plagioclases with high temperature optics are found in effusives, and also, on account of anomalous extinction angles, in some specimens of plutonic rocks. It is also possible that the albite phase of the cryptoperthites may have high temperature optics, because Chao (1939, p. 342) found that the X-ray rotation photograms showed different patterns for ordinary albite and the albite phase of the cryptoperthites.

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DISCUSSION

A. K. Wells referred to the importance of the author's conclusions especially with reference to their repercussions on petrographic classification and nomenclature. He asked for information on two points: first, the relationship of the feldspars now described to those called anorthoclase from the kenytes of East Africa and Antarctica; and secondly, the ratio of plagioclase to alkali-feldspar in the larvikite. If the plagioclase has the status of an accessory mineral only, in some phase of larvikite, the name can be retained with its original significance; but if *all* larvikite contains essential plagioclase to the extent of one-third or more of the total feldspar, then there is no alternative to classifying the rock as a syenodiorite. It is much to be hoped that some portion of the complex is larvikite in Brögger's original sense; but obviously a new name must be found for the plagioclase-rich monzonitic facies.

C. Oftedahl (in reply): The so-called " anorthoclase " of the rhomb-shaped phenocrysts in the Oslo rocks is either plagioclase or antiperthite. The author has only seen a few slides from the rhomb-porphyries of East Africa and Antarctica and he is inclined to consider the rhomb crystals of these rocks similar to the Oslo phenocrysts.

The *larvikite* is a *monzonite* with approximately 50/50 plagioclase-cryptoperthite. In the special dark schillerizing variety the two phases form a coarse microperthite, but there is gradual transition to the ordinary larvikite with two kinds of feldspar individuals; therefore even the dark variety is called " monzonite."

GRANITES OF MÓRÁGY, HUNGARY

By F. PAPP
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ABSTRACT

140–150 km. SSW of Budapest, there are remains of Variscan orogeny hardly surpassing 300 m. elevation built up of amphibole-biotite granite locally passing into granodiorite or, in one place, into syenite.

Composition of the granite: Quartz 30–55 volume per cent, Orthoclase 13–55 per cent, Microcline 6–41 per cent, Oligoclase 1·6–10 per cent, Biotite 1–15 per cent. Chemical analysis: SiO_2 71–77 per cent, Al_2O_3 12–14·6 per cent, Fe_2O_3 0·75–2 per cent, K_2O 4·82–7·67 per cent, Na_2O 2–3·75 per cent. Mineral and chemical composition of the granodiorite: Quartz 16–51 per cent, Orthoclase 5–24 per cent, Oligoclase 12–67 per cent, Biotite 1–10 per cent, Amphibole 0–39 per cent, SiO_2 52–62 per cent, Al_2O_3 11–17·46 per cent, Fe_2O_3 + FeO 4–8·8 per cent, CaO 4·3–8·33 per cent, K_2O 1·6–8·3 per cent, Na_2O 1·6–4·48 per cent. Mineral composition of syenite: Orthoclase 40 per cent, Amphibole 42 per cent, Quartz 8 per cent, Titanite 5 per cent, Biotite 5 per cent.

Aplites, quartzites and basic segregations occur in connection with these rocks, which have to be classed as transitions into alkali rocks.

Surface strata of the region are composed of Lower Pliocene (Pannonian) sands and clays and of Pleistocene Loess. Argillaceous shale devoid of fossils at the contact of the granite indicates the presence of a laccolite. The deeper substratum is not known.

CHARBONS ET PÉTROLES

By A. RENIER
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ABSTRACT

Ses progrès dus aux plus récentes observations aboutissent, semble-t-il bien, à la confirmation de l'étroite parenté originelle de ces substances en apparence si dissemblables à qui ne considère que les modes d'exploration ou d'exploitation. De part et d'autre, accompagnement de gaz et d'eaux similaires. Des essais de cokéfaction progressive des houilles belges ont montré que, pour 80 pour cent, leur substance est la même,—disons un bitume pour parler comme C. Eg. Bertrand devant le Congrès de 1900—et ce quel que soit leur degré d'anthracitisation. La substance fondamentale a pénétré dans les cellules végétales, comme dans les loges des Céphalapodes, par un processus d'allure filonienne. Ainsi que David White l'a exposé la différence entre charbons et pétroles résulte, en principe, du mode d'évolution.

ON THE GENESIS OF PERALKALINE ROCK PROVINCES

By EGIL SAETHER

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ABSTRACT

The paper attempts to explain the formation of peralkaline magmas through diffusion processes in a magma mass with extraordinarily great vertical extension. It is pointed out that, in such a mass, in the state of equilibrium the concentration of each component will vary with the altitude in a way similar to that of the gases in the atmosphere. Volatiles in the magma (H_2O, CO_2, Cl, F, fluorides of Ti, Zr, and Nb) will be enriched at the top of the magma chamber; a method of estimating the degree of enrichment is given.

Next it is demonstrated how the volatiles, through their acid character, will attract basic ions (Na^+, K^+, Ca^{++}, and Ba^{++}) and enrich them at the top of the chamber. Here a peralkaline magma, rich in CO_2 and other volatiles, will be formed. Its alkalinity will be more pronounced, the greater the vertical extension of the original magma chamber was.

The theory here outlined seems to explain several as yet enigmatic features in the chemistry and mode of occurrence of the peralkaline eruptives (examples are given from recent investigations in the Fen district, Norway). It is indicated how the theory can be further tested.

INTRODUCTION

THE present paper is chiefly incited by my field experience in the Fen district in Norway. This is a small area of peralkaline rocks situated 120 km. S.W. of Oslo. The rock assemblage, which has been petrographically described by W. C. Brögger (1921), comprises coarse-grained, amphibole- and calcite-bearing pyroxenite (vipetoite), rocks consisting of pyroxene and nepheline in different proportions (melteigite, ijolite, and urtite), pyroxene-calcite- and pyroxene-nepheline-calcite-rocks, nearly pure calcite rock (sövite), ankerite rock (rauhaugite), and carbonate-haematite-rock "rödberg": "red rock"). The area is surrounded by a zone of alkali syenite (fenite), which has been formed from Archaean gneissose granite through alkali metasomatism.

My own recent field work in this area has chiefly aimed to reveal the contact relations between the different rocks, and thereby their genesis. The results will be described in a future paper, here only the principal features can be stated briefly.

There has been a magma, very poor in silica and rich in alkalies and lime. It has been extremely rich in volatiles, in particular CO_2. It has had the temperature of an ordinary magma. It has been very fluid, and had a pronounced facility of imbuing the granitic bedrock and transforming it into alkali syenite. Through crystallization the magma has produced pyroxene-nepheline rocks, mixed silicate-carbonate rocks, and calcite rocks. At a stage of more advanced cooling it has expelled hydrothermal carbonate solutions, which have continued to form calcite rock, and also metasomatically transformed parts of the silicate rocks into calcite rocks. Later, at a still somewhat lower temperature, ankerite has been formed instead of calcite. At last the carbonate-haematite rock has been formed in connection with rapid escape of CO_2 through fissures.

The Fen district is an example of an eruptive rock province of extreme alkalinity. A great number of similar provinces are known from different parts of the world. They are mainly characterized by the occurrence of pyroxene-nepheline rocks, together with nepheline syenite and aegirite syenite (fenite and related types). The silicate rocks are very often associated with carbonate rocks. In many of the peralkaline rock provinces are enriched large quantities of F (in fluorite and apatite), Cl (in sodalite), P (in apatite), Nb (in pyrochlore minerals), Ti (in titanite and melanite), Zr (in zircon, eudialite, a.o.), and Ba (in baryte and hyalophane).

The genesis of the peralkaline rock provinces has for a long time been one of the most disputed

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problems in petrology. The numerous attempts which have been made to explain their genesis, have mainly been based on the following processes:

(1) Differentiation through fractional crystallization of a basaltic or peridotitic parent magma. This parent magma has either been assumed to be very basic from the beginning (Holmes, 1931) or the unusual course of the differentiation has been ascribed to a primary high content of volatiles in the magma (Smyth, 1927).

(2) Contamination by limestone in the parental (basaltic) magma, which has thus been desilicified (Daly, 1933; Shand, 1930).

(3) Metasomatic introduction of alkali in older (igneous or sedimentary) rocks (Wegmann, 1937; Eckermann, 1942).

The theory suggested in the present paper is based on diffusion processes in a magma mass of great vertical extension, effected by the differences in pressure in different levels in the magma. In my opinion, the process 2 stated above, though it may have been active in the evolution of some alkaline rock provinces, cannot give a general explanation of provinces of the Fen district type. These are in many cases intruded in granite and gneiss complexes with no trace of limestone layers. The process 3 has undoubtedly been active in the Fen district and related areas, but cannot be regarded as being the primary process. The high alkali concentrations which are needed to effect the metasomatism in question must have some source, and the central problem is then to find this source.

THE VERTICAL DISTRIBUTION OF THE DIFFERENT COMPONENTS IN A LIQUID MASS

It is well known that in a mixture of different gases (e.g. the atmosphere) the composition of the mixture is not the same in different levels when the mass is in gravitational equilibrium. The partial pressure of the heavier components will decrease faster with the altitude than that of the lighter ones, and the heavier gases are thus enriched at the bottom of the mass, the lighter ones at the top.

In a mixture of liquids similar conditions will exist, and the mass will not be homogeneous when being in gravitational equilibrium. The conditions are, however, far more complicated here than in the gas phase, and the behaviour of the different components cannot be deduced from their specific gravity nor their molecular gravity. Only for components which have a limited solubility in the liquid, can the theory at present be worked out.

When a substance (liquid or solid) is limitedly soluble in a liquid, its solubility will, as a rule, depend on the pressure. If it increases with increasing pressure, the substance in question will be more soluble at the bottom of the liquid mass than at the top of it, and opposite if the solubility decreases with increasing pressure. If the solution is undersaturated, the actual concentration of the substance in any level is proportional to its solubility in the same level, according to the law of distribution. This law is strictly valid if the solubility of the substance is low (e.g. gypsum in water), but only approximate if the solubility is high (e.g. NaCl in water). Any substance which is dissolved in the liquid under volume contraction, and is consequently more soluble under high pressures than under low ones, will be enriched at the bottom of a deep liquid mass. If the concentration curve is disturbed through stirring of the liquid, it will be re-established through diffusion of the substance.

The conditions outlined here may possibly be investigated experimentally by means of an ultra-centrifuge, if expedient experimental substances are chosen.

ENRICHMENT OF VOLATILES AT THE TOP OF A MAGMA MASS

In magma masses the conditions outlined in the previous chapter must be supposed to be very important. The vertical extension of a magma chamber may be estimated to 10-100 km., in some cases perhaps still more, and great pressure differences will exist between its upper and lower parts. As most of the components in a silicate melt are unlimitedly miscible, nothing can, however, at present be said of their possible enrichment at the top or bottom of the magma basin. But one category of substances, viz., the volatiles, have only a limited solubility in the melt, and their solubility is very much

dependent on the pressure. The volatiles must, therefore, be expected to exhibit very pronounced enrichment effects due to the pressure variations in a magma basin.

We imagine that a semi-permeable vertical tube (the walls permeable to gas, but not to liquid) is placed in a basin filled with a liquid with a gas in solution (Fig. 1). This tube will be filled with gas, and the pressure of the gas in any level will be the sum of the pressure at the top of the tube and the weight of a gas column from the top down to the level concerned. At the top the pressure of the gas is like or lower than that of the surrounding liquid (like, if the solution is saturated and the roof of the basin is impermeable both to gas and liquid), in any other level it will always be lower (see the curves of Fig. 2). In any level there will be equilibrium between the gas in the tube and the gas dissolved in the liquid, so that no gas circulation takes place. Such circulation would namely carry heat from one part of the liquid to another, and thus violate the second law of thermodynamics. It can be concluded that the solubility of the gas in the liquid must depend on the altitude in such a way that equilibrium will exist between the gas solution and the gas in a semi-permeable tube which may be brought into the liquid.
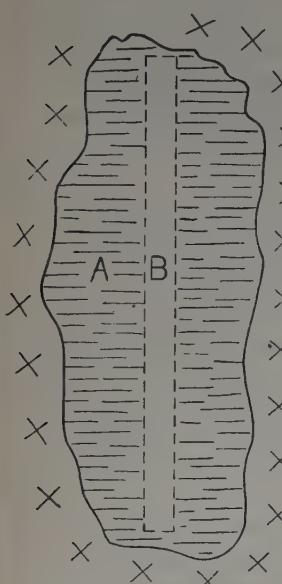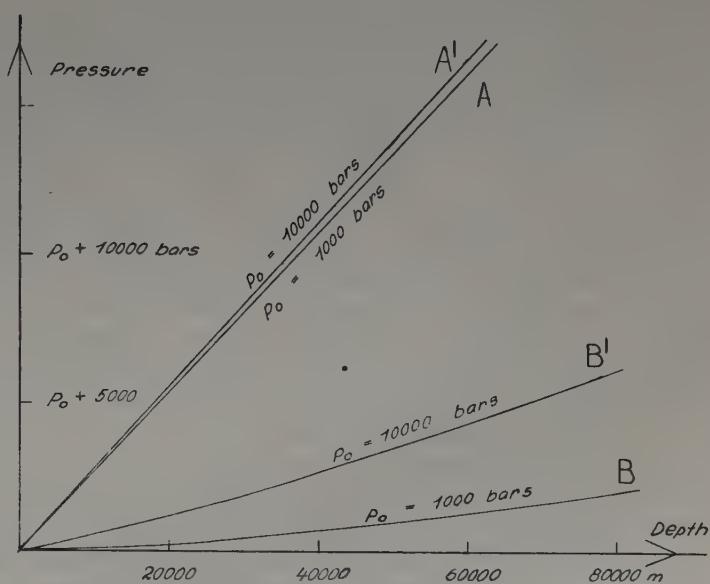

Fig. 1   Fig. 2

FIG. 1.—*Illustration of the deduction of the solubility of a gas in a liquid in different levels.*
   A: Liquid. B: Semi-permeable tube filled with the gas in question.

FIG. 2.—*Graphical representation of the pressure in an albite melt (A–A') and in water vapour (B–B')*
   in different levels at a temperature of 1000° C.
   The gravity of the melt is supposed to be $2\cdot6$ $(1 + 0\cdot000005\ p)$, p in bars; that of the vapour is calculated from the approximate equation: $p(V \div v_0) = RT$. (v_0 is the volume of 1 mol. of water in the liquid state). The pressure p_0 at the top of the liquid and vapour mass is supposed to be 1,000 bars (the curves A–B) and 10,000 bars (A¹–B¹).

The conditions of equilibrium between a gas phase and a liquid which contains the same gas in solution, have been theoretically investigated by R. W. Goranson (1937). He finds that, under constant pressure in the gas phase, the solubility of the gas in the liquid decreases rather rapidly with increasing pressure in the liquid (see the curves of Fig. 3, which are drawn from the solubility values given by Goranson). Fig. 4 illustrates the solubility of water vapour at different levels in an albite melt at a temperature of 1,000° C., computed from Goranson's figures and the pressure values taken from Fig. 2. It is seen that the solubility is 2-3 times as high at the top of the liquid mass as at a 5 km. deeper level.

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If the gas solution is undersaturated, the actual concentration of the gas at different levels will be (at least approximately) proportional to the solubility at the same levels, and the gas will be enriched at the top in a similar manner to that shown in the curves of Fig. 4. If the solution is supersaturated, it will boil and give off gas at the top of the liquid mass (boiling takes place when the tension of the dissolved gas exceeds the pressure of the liquid, so that gas bubbles can be formed). It is worthy of emphasis that boiling can never begin in deeper levels, although the gas solution is supersaturated throughout the liquid mass. In deeper levels the pressure of the liquid is always higher than the gas tension, and bubbles cannot be formed. The excess of gas in deeper levels can only escape through diffusion to the upper levels.
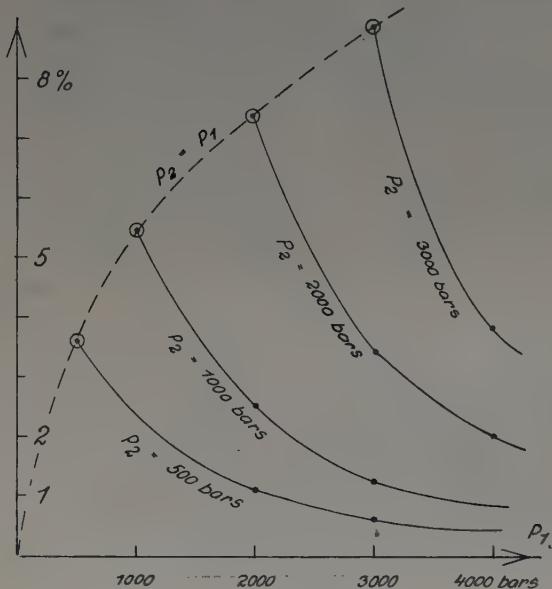

Fig. 3
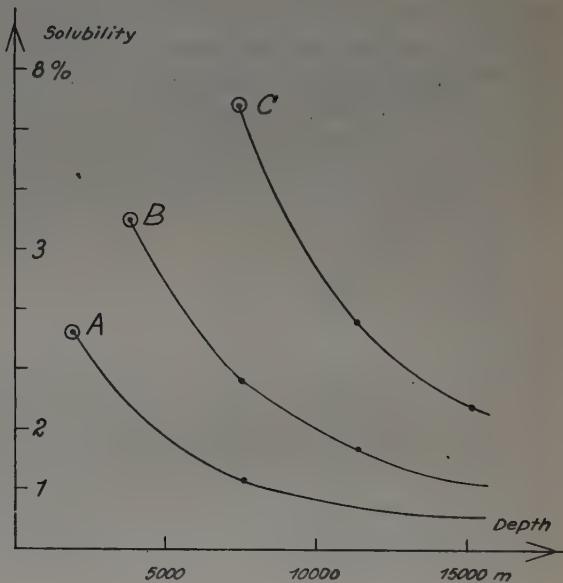
Fig. 4

FIG. 3.—*Curves which illustrate the solubility of water vapour in an albite melt at a temperature of 1000° C. under different pressures on the melt* (p_1) *and on the vapour phase* (p_2).

FIG. 4.—*Curves which illustrate the solubility of water vapour in different levels in albite melt masses, the tops of which are assumed to be situated* 2000 m. (*A*), 4000 m. (*B*), and 8000 m. (*C*) *below the earth's surface, and covered by roofs impermeable to the vapour.*

The pressures acting on the melt and the vapour in a certain level are taken from the curves of Fig. 2, and the solubility of the vapour then taken from Fig. 3.

It may be mentioned that, as the solution of gas in a magma is an exothermic, and expelling of the gas an endothermic, process, the enrichment of gas at the top of a magma mass will be accompanied by a heat transfer in the same direction. The upper part of the magma will thus be heated, the solubility of the gas lowered, and the gas enrichment counteracted. But as the heat conduction in a liquid is a more rapid process than the diffusion of a dissolved substance, the temperature difference will soon be smoothed out so that the gas enrichment can continue, and the final result will not be influenced.

It will probably be rather easy to make at least a qualitative test of the theory outlined above by means of an ultracentrifuge. In a centrifugal field of about 10,000 times the force of gravity easily measurable differences between the concentration of e.g., a solution of CO_2 or NH_3 in water in the upper and lower part of a vessel of a few cm. in height should be expected to occur. To carry out the experiment with silicate melts will be difficult.

There is reason to believe that gas enrichment at the top of a magma basin plays a very important rôle in the volcanoes. In all volcanic eruptions the expelled quantity of gas (mainly water vapour) is immense, and in some cases it is even estimated to exceed the quantity of lava and ashes in weight. These immense gas quantities are, in my opinion, not normal constituents of the magma, but the result of local gas enrichment where the magma rises near the earth's surface. The enrichment will be more pronounced, the higher the magma rises. At last the gas tension will be able to lift the remaining rock roof; a violent eruption can then take place. The pressure at the top of the magma mass sinks to 1 atmosphere, and the upper, gas-loaded part of the magma boils until the excess of gas is given off. The gas in the deeper parts of the magma will now diffuse upward and re-establish the enrichment at the top, and thus cause continued boiling here. As the diffusion is a slow process, the boiling may continue for a very long time, perhaps for millions of years. The long-lasting rhythmical activity of volcanoes may be explained in this way.

It is also evident that the gas enrichment will influence the course of crystallization and differentiation of the magma. The importance of the water content of the magma to these processes has been pointed out by Goldschmidt (1922). He pointed in particular to the characteristic difference between the opdalite-trondhjemite kindred and the anorthosite-charnockite kindred, the former having had a " wet ," the latter a " dry " parent magma. Now the rocks of the former kindred are assumed to have been formed under hypabyssal conditions (concluded e.g. from the repeated recurrent zoning in their plagioclase), the latter under typically abyssal conditions (regularly associated with eclogites and granulites). This is in full harmony with the theory of an upward diffusion of the volatiles in a deep magma basin.

FORMATION OF PERALKALINE ROCKS THROUGH ENRICHMENT OF CARBON DIOXIDE AT THE TOP OF A MAGMA

It is my conclusion that peralkaline rocks are formed through upward enrichment of CO_2 in a very deep-seated magma basin with great vertical extension. This conclusion is supported by the frequent association of these rocks with magmatic and quasi-magmatic (hydrothermal) carbonate rocks, and with rocks of the kimberlite-alnöite-damtjernite group. Also their richness in F, Cl, and elements which form volatile halogenids (P, Ti, Zr, Nb) indicates that they have been formed at the top of a magma basin. The parent magma may have been basaltic or peridotitic (kimberlitic).

Since CO_2 is a gas whose solubility in magma is dependent on the pressure in a way similar (at least qualitatively) to that of the water vapour, it will be enriched at the top of any magma mass with great vertical extension. Its solubility under different pressures can be computed after the method of Goranson, when the necessary constants are determined, and then also the degree of enrichment can be computed. This is an important task in order to throw light on the problem here concerned.

The conditions in nature must be supposed to be complicated, as CO may also be formed, and a chemical equilibrium exist between CO and CO_2 ($CO_2 + 2FeO \leftrightarrows CO + Fe_2O_3$). In very great depths also elementary C may be formed (cf. the occurrence of diamond in kimberlite).

CO_2 has another important property: it can react with water and form an acid, which dissociates in the ions H^+, HCO_3^+, and CO_3^{++}. At magmatic temperatures the degree of dissociation is high, and a large quantity of CO_2 dissolved in a magma will produce a rather high concentration of H^+-ions. The ions will have a tendency to diffuse downward in the magma (the concentration being much higher at the top than in deeper levels), and the stationary state in the magma will thus be a dynamic equilibrium between an upward diffusion of CO_2 molecules due to the difference in pressure between the higher and deeper levels, and a downward diffusion of ions due to the concentration gradient. Now the H^+-ions have a much higher rate of diffusion than the heavier ions, and will diffuse downward in advance of the CO_3^{++} and HCO_3^+ ions. An upward-directed electric field will thus be produced. This field will retain the downward diffusion of the H^+-ions and aid that of the anions, and thus prohibit separation of the two sorts of ions.

Hitherto I have reasoned, as if carbonic acid had been the only dissociated substance in the magma. The final result would then be that the total concentration of CO_2, HCO_3^+, and CO_3^{++} became

constant in time and a certain function of the level, with a maximum value at the top of the magma chamber. A vertical electric field, likewise constant in time and a function of the level, would be established. The magma contains, however, many other ions, viz., the negative silica ions and the positive ions of Na, K, Ca, Mg, etc. All these ions will be affected by the electric field which is established through the upward enrichment of carbonic acid. The silica will be drawn downward, the kations upward. According to well-known experience in electrolysis of silicate melts the silica is nearly immobile, while the kations, and especially Na^+ and K^+, but also Ca^{++}, are easily moved by an electric field. The result is, consequently, that the strong bases (alkali and lime, and together with them baryte) are enriched at the top of the magma chamber together with the carbonic acid. Popularly it can be said that the carbonic acid repels other acids, and attracts bases. No quantitative theory can be worked out here. The many different substances will influence each other's activities in a very complicated way, and the complexity of the process and the great number of unknown factors prohibit any attempt at calculation. Also the concentration curve of the carbonic acid in different levels will be influenced in a way which is difficult to predict.

The qualitative theory outlined here can, however, be checked experimentally by means of an ultracentrifuge. It must here be worked with acid- or base-forming gases (SO_2, NH_3) together with non-volatile acids and bases in water. To experiment with silicate melts will be extremely difficult.

We have now seen that at the top of a deep-seated magma mass there is a possibility for having formed a magma which is highly enriched in:

(1) Volatiles: H_2O, CO_2, HF, HCl, fluorides of P, Ti, Zr, and Nb.

(2) Strong bases: Na_2O, K_2O, CaO, BaO.

This magma has the same composition as the magma which must have formed the peralkaline eruptive provinces of the Fen district type.

The conditions for having formed such a peralkaline magma must, however, be rather peculiar. Firstly, the vertical extension of the magma mass must be great enough to effect a material enrichment of CO_2 at the top. As the solubility of CO_2 in silicate melts under different pressures on the gas and the melt has not been studied, no statements on the absolute value of the necessary height can be made. The concentration of CO_2, and the resulting alkalinity of the top magma, will be more pronounced, the greater the height of the magma chamber is. Secondly, the top of the magma mass must stay in an approximately constant level for a very long time (certainly many millions of years), so that both the enrichment of CO_2 and the following enrichment of alkali and lime can take place undisturbed. This involves:

(1) The process must take place in a deep level in the earth's crust. No magma, and in particular not one which is loaded with volatiles, can stay in constant level for a long time near the earth's surface. It will here sooner or later find its way to the surface, or expel the volatiles through fissures, or cool and crystallize.

(2) The geological milieu must be stable; in particular orogenic movements must not take place. In active orogenic zones the diffusion processes will always be disturbed; at most the water can be enriched to some extent, so that it can cause the usual volcanic phenomena (as the water has lighter molecules than the carbonic acid, it will have a higher rate of diffusion). On the whole we arrive at the conclusion that peralkaline rocks can only be formed in stable parts of the earth's crust, outside active orogens. This is in full harmony with our field experience on these rocks.

The peralkaline magma which is formed near the roof of a deep magma basin, will have a temperature similar to that of the basaltic (or peridotitic) parent magma, or perhaps somewhat higher, owing to the thermal effect of the gas transfer. This temperature is higher than the lower liquid temperature of a granite, and the peralkaline magma will, therefore, have a pronounced chemical reactivity toward granitic rocks (which usually constitute its country rock). The granitic rock will be assimilated, and a heterogeneous group of nepheline syenites and related rocks will be formed. In some cases the assimilation processes may proceed so far that the primary peralkaline rocks (urtite, ijolite, etc.) are not developed at all.

The extremely high content of CO_2 and other volatiles in the peralkaline magma also makes it understandable that the country rock is imbued in a considerable distance from the magma, and e.g., granite transformed into alkali syenite (fenite, umptekite).

When the peralkaline magma is cooled, the volatiles will form a hydrothermal phase, which generates hydrothermal carbonate rocks, and also can react with already consolidated silicate rocks.

THE POSSIBILITY OF TESTING THE THEORY DEVELOPED IN THE PRESENT PAPER

As stated in the foregoing the theory seems to explain many of the peculiarities of the peralkaline rocks:

(1) That they only occur in stable parts of the earth's crust, outside active orogenic zones.

(2) That they are often associated with kimberlite and related rock types (alnöite, damtjernite), which are commonly assumed to be derived from very great depths.

(3) That they are often associated with carbonate rocks.

(4) That they are rich in F, Cl (volatiles), Ti, Zr, P, and Nb (elements with volatile halogenids).

(5) That they are rich in Ba, and in some cases (Alnö) accompanied by baryte dykes.

(6) That they are surrounded by zones of rocks formed through alkali metosomatism in the country rock.

In order to have the theory further tested, the following investigations must be carried out, as stated in the previous chapters:

(1) Experimental work (by means of an ultracentrifuge) on the vertical distribution of a volatile substance dissolved in a liquid, and on the effects of a local concentration of an acid-forming gas on the distribution of other dissociated solutes.

(2) Determination (after the method of Goranson) of the solubility of CO_2 in silicate melts under different pressures on the gas phase and the melt.

(3) Determination of the rate of diffusion of the different components, in particular the volatiles, in silicate melts.

(4) Detailed geochemical investigation of peralkaline rock provinces, in order to get a complete record of which elements are enriched in relation to their occurrence in normal granitic and basaltic rocks. The theory demands that the enriched elements shall belong to one of the following categories:

    (*a*) Elements which easily form volatile compounds.

    (*b*) Elements which form strong bases with mobile kations.

(5) Detailed field work in as many peralkaline rock provinces as possible. In particular the mode of occurrence of the accompanying carbonate rocks must be investigated very elaborately, in order to make clear their genesis (magmatic, hydrothermal-metasomatic, included fragments of sedimentary limestone). Likewise, it will be important to search for indications of a metasomatic genesis of some of the silicate rocks (e.g., nepheline syenite and ijolite, such as is pointed out by Eckermann in the Alnö district).

PROBLEMS IN CONNECTION WITH THE THEORY

It is easily seen that the theory is based on the view that the earth is solid down to great depths, and that individual magma basins may be formed through local fusion. This view is strongly supported by geophysical experience, and will be furthermore supported, if my theory should be confirmed by future research.

An important problem is the origin of the CO_2, which, in the theory, plays a dominant rôle in the genesis of peralkaline rocks. It is a fact that CO_2 is a very common constituent of volcanic gases, and the presence of the element C in great depths is indicated by the occurrence of diamond in the kimberlite pipes. In some cases the CO_2 in the magma may have been derived from assimilated limestone, and some alkali rock provinces may have been formed in this way, but, as stated in the introduction, it can hardly be any general explanation. It is probable that carbonates (or elementary carbon, which readily forms CO_2 through reaction with Fe_2O_3 when the rock is fused) have a wide distribution in the deeper parts of the earth's crust.

J

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DISCUSSION

H. VON ECKERMANN: According to Dr. Saether's representation hydrogen should diffuse downwards. That must lead to a corresponding water concentration, while the evidence at Alnö indicates the opposite. Neither is there any Na concentration upwards as postulated by Saether.

The Alnö alkaline occurrence being the almost exact counterpart ôf Fen in Norway (the former representing, however, a higher level of the intrusion) the probability of Saether's hypothesis may be tested by comparison with Alnö. In that light it does not seem very probable, the genesis certainly being more complicated both at Alnö and Fen.

The occurrence of CO_2 and other volatiles both as vapour and as part of the melt, must be taken into account, the ratio being determined by the temperature, pressure and concentration, viz., equilibria of all the components of the melt.

A. STRECKEISEN asked concerning the source of the considerable amount of CO_2 in peralkaline rocks. Why are there deep-seated magma-chambers rich in CO_2 which produce the peralkaline rocks, and why are other magma-chambers, deep-seated too, poorer in volatile substances and producing the rocks of the ordinary calc-alkaline rock suite?

C. E. TILLEY: What is the mode of origin of the carbonate dikes in the Fen District of Norway?

E. SAETHER (in reply): My reasoning on the migration of the CO_2 is based on the fact that the solubility of CO_2 in magma is dependent upon the pressure in such a way that it is dissolved at high and expelled at lower gas pressure. It does not matter in which form it is actually present in the solution (CO_2 molecules, carbonate molecules, ions, CO molecules, or elementary C).

The downward diffusion of H^+ ions will only slightly alter the feature that the water is concentrated in the top portion of the magma together with the carbonic acid.

The Fen district is more deep-seated than the Alnö district, and most of the differences between these districts can be explained hereby. In the Fen district we have no signs of explosive volcanism, and no cone sheets. There is clear evidence that parts of the carbonate rocks have been formed through metasomatism of silicate rocks.

There is no essential difference between magma masses which form peralkaline rocks and the other magma masses. The former have, however, had great enough vertical extension and long enough time to develop alkalinity in the top portion. The chief condition for this is situation in a stable part of the earth's crust.

I have made no definite statements on the origin of the CO_2. It may in some cases be derived from assimilated limestone, but I would rather assume a wide distribution of carbonates in the deeper parts of the earth's crust.

There is evidence that the " dikes " of carbonate rock in the Fen district have been formed through pressing of the carbonate into fissures in a solid, but plastic state (like " boudinage " in sediments).

ON THE ANATECTIC DIFFERENTIATION IN GRANITIC AREAS

By K. SMULIKOWSKI

Poland

ABSTRACT

Each of the main processes of rock-formation has its own mode of differentiation, controlling the repartition of different chemical elements within the earth-crust. The same may also be said about the process of anatexis of rocks in deeper levels of the sialic zone. The resolution of various minerals and rocks constituting a given rock-complex, must be fractional and gradual, separating more fusible materials from the more refractory ones.

For a convenient classification of the products of anatexis some special petrogenetic terms seem to be needful: (1) *Palingenites*—products of the secondary melt originating by anatexis, (2) *Lipotectites*—solid remainders of the primitive rock-complex, (3) *Diachytes*—rocks relaxed by partial refusion, with abundant refractory crystals swimming in a palingenetic medium (transitional between 1 and 2). Lipotectites may be divided into (*a*) *Atectites* not at all affected by the liquefied portions and (*b*) *Metatectites* more or less altered by the action of mobilized fluids. The anatectic series: *Atectites, Metatectites, Diachytes, Palingenites*, may show a mode of differentiation very similar to a pure magmatic suite.

Very instructive examples of such anatectic differentiation are found in the Archaean granitic areas of Volhynia and they may be illustrated by suitable graphs.

IT is beyond any doubt nowadays that the granites and allied acid deep-seated rocks can originate in a secondary way, by essential transformations of some other, especially sedimentary rock-masses. The last decades have furnished many examples from different countries, proving irrefutably such a possibility. Serious dissentions, and even contradictions exist, however, concerning the mechanism and the causes of secondary granite-forming processes within the Earth's crust. Endless discussion upon this problem in geological world literature did not succeed in reaching agreement with regard to fundamental ideas in this matter.

One group of petrologists considers the granites as products of metamorphism and metasomatism of sedimentary rocks (" *Granitization* "), by action of some emanations surging from beneath (" *Rheomorphism* " of Backlund). Stating incontestable proofs of mutual replacement among the minerals of many granitic rocks, they do not believe in the existence of any notable amount of fluid phases in them and they question the occurrence of any granitic magma within the Earth's crust. The other group referring to the tradition of classic igneous petrology, accept the generation of fluid granitic magmas in the depths of the lithosphere evidenced, in their opinion, in intrusive contacts and in volcanic eruptions of acid lavas. These magmas could originate partly from melts remaining after fractional crystallization of basaltic magmas, partly from initial fractions of secondary remelting of some pre-existent rocks (including sediments).

Both kinds of views upon the origin of granites, mentioned above, are usually sharply opposed. The author does not understand why they should be considered as contradictory and why they should exclude one another. During many years of petrological work in the granitic areas of Volhynia (1946), he was able to investigate innumerable examples of granitization and mineral replacement in a solid condition, and nearby also many signs of magma-bearing liquefaction of some rock-fractions. In consequence he was led to the opinion, that in the granitic areas of that country both granite-forming processes were superposed one upon another in the time-sequence, and contributed jointly to the important complexity of these areas. Moreover he thinks that only a suitable combination of both ways of granite-formation can create a right basis for the interpretation of the whole granite-problem.

The granite-bearing activization of an orogenic belt begins probably by the afflux of emanations from the substratum, granitizing sedimentary complexes in a metasomatic way, without any notable liquefaction (" Rheomorphism "). Such emanations can hardly be regarded as anything else than a mobilization of more volatile compounds of the substratum, owing to the rise of their vapour-tension on account of increasing temperature. The ascent of geo-isotherms in the geo-synclinal complex extends the reach and the grade of its granitization. This ascent leads finally to partial mobilization of liquid phases, i.e. to " *differential anatexis* " in the sense of Eskola. At first only the most fusible compounds of the complex fall victim of that liquefaction, later on gradually others are included, contributing to the origination of a *palingenetic granite-magma*. Thus the swelling granitization (" *Migmatite-front* " of Wegmann) spreads more and more, preceding and preparing the subsequent flood of anatexis and palingenesis; both the latter, however, promote the front of granitization further and further supporting and reviving their granitizing emanations.

The primitive rock-complex which is the scene of those transformations may be composed of very different materials such as sedimentary strata of various kinds, with some intercalations of basalt or diabase, subsequently metamorphosed into crystalline schists or gneisses with some beds of amphibolite or hornblende-hornfels. It is not very probable, that any granitizing metasomatism could efface completely such contrasts of composition. Posterior anatexis begins with the solution of only those rock-components of the metamorphosed complex, which are of a most susceptible composition (rich in alkali-feldspars). More basic rocks, as amphibolites or hornblende-hornfelses, resist its action obstinately and are left in a crystalline state. Thus during the anatexis the rock-complex splits into dissolved fractions furnishing an acid and alkali-rich palingenetic granite-magma and, on the other hand, in some alkali-poor and more basic fractions, rich in lime, iron and magnesia. The former called *Palingenites*, lose entirely their primitive textures, reaching the condition of a secondary magma. The latter may be called *Lipotectites* (i.e., saved from re-fusion); they conserve their primitive meta-morphic textures, which, however, may become less and less conspicuous in the course of advancing recrystallization.

A schematic picture of such processes is offered in Fig. 1. A further progress of differential anatexis at rising temperature liquefies greater and greater masses of the whole rock-complex. Components more and more rich in lime and magnesia pass to the palingenetic magma, and thus the lipotectites are gradually reduced to the most refractory rock-components. They can maintain in part their primitive unaltered condition, owing to their mineral composition and very coherent texture (*Atectites*). More often, however, they are impregnated by the surrounding palingenetic magma, and subjected to gradual granitization (*Metatectites*); thus they may become less refractory and may relax slowly, setting free their mafic compounds as epidote, hornblende, biotite or calcic plagioclases. The palingenetic magma thus becomes contaminated with crystals of these minerals, acquiring an inter-mediate composition (*Diachytes* = relaxed rocks). Loose crystal-aggregates of such origin are called *Mianthites* (staining elements); bigger and compact fragments of torn lipotectites give dark melanocratic enclosures in palingenites.

A subsequent folding of those mobilized half-liquid masses within an active orogenic belt sets them in an upward flowing motion. Shallower levels affected only by a metasomatic granitization or, at best, invaded by granitic secretions pressed from beneath (migmatites), cannot be distinctly differen-tiated during that motion. They constitute a plastic, but really not fluid *migma*, pressed in an inert state in superior structures of the rising mountain-chain, as batholith-like domes. The variability of composition is due partly to primitive differences in the granitized rocks, partly to superinduced metasomatic changes.

However, the flood of anatectic masses liquefied in a high degree surges underneath. In a fluid granite-juice float abundant crystals of undissolved and more refractory minerals. In various grades of fluidity those masses are submitted to a differentiation during their motion: more liquid portions flow more quickly than those overburdened with crystals. The granitic fluid is squeezed from the mush, leaving the crystals condensed in lenticular nests stretched in the flow-direction of the whole anatectic

complex. In the same manner are also disposed the undissolved lipotectites, as remnants of amphibolitic intercalations in the primitive rock-complex.

Such a picture of fluidal tectonics is presented, in the opinion of the author, by Archaean granitic areas, investigated by him in North Volhynia (environs of Klesów, Tomaszgród, Wyry and Rokitno). The main rock-ground of these areas consists in pink leucocratic, mostly fine-granular granites (aplogranites and microgranites), in which numberless shreds, lenses or nests of coarser grain are loosely suspended with mostly parallel strikes E.—W. or N.E.—S.W. All these rocks exhibit true consolidation-structures, and their ability to penetrate the solid materials with narrow
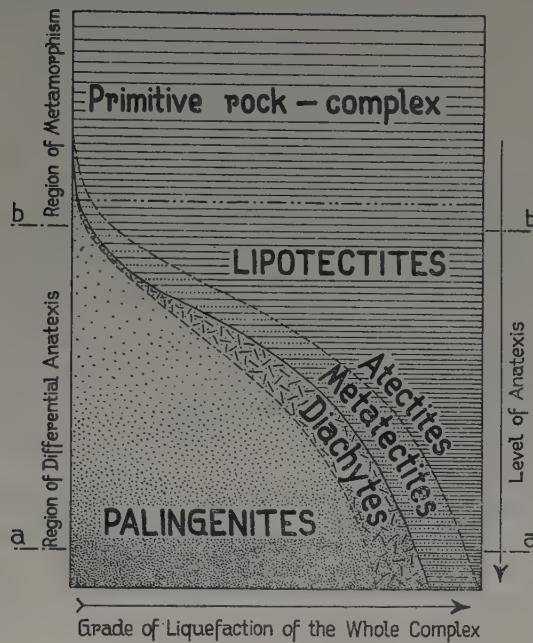

fig. 1

Classificatory Scheme of the Products of Anatexis

veins speaks also in favour of their fluid origin. They are widely differentiated in their composition, offering a distinct. and continuous rock-series from hololeucocratic and potash-rich *aplogranites*, over *common granites, adamellites* and *granodiorites* to *syenodiorites*. The latter rock-group is marked mostly by a coarse hypautomorphic grain and composed chiefly of big closely packed oligoclase or andesine crystals with distinct signs of protoclastic deformation. They look as if they were local accumulations of plagioclase, like anorthosites.

The whole series show characteristics of true magmatic differentiation by crystal-sorting of plagioclases with minor amounts of mafic minerals (hornblende and biotite). The one pole of that series is realized in the syenodiorites, enriched in less fusible compounds, the other pole is given by alkali-aplogranites, rich in quartz and alkali-feldspars as minerals of rest-crystallization.

Relying on these arguments the classic petrology of igneous rocks would be inclined to consider the whole series of pink granites of Volhynia as products of true and primary magma. This would be, however, certainly wrong, because amidst those granitic masses there are many concordantly disposed intercalations of dark-coloured lipotectites, with very characteristic structures showing that they have never been fluid, but were conserved as metamorphic hornfelses or amphibolites. They offer many symptoms of metasomatism and granitization, but they have not been incorporated in the magma. The surrounding granites penetrate them with numerous veins and tear them in pieces forming dark

enclosures. Sometimes the lipotectites are loosened in mianthitic aggregates of mafic minerals, contaminating the granites and producing diachytic types. But even then many traces of relic-textures may be observed, proving their non-magmatic origin.

Lipotectic intercalations among the red granites may be also arranged in a continuous petrologic series with apparent signs of true magmatic differentiation: *hornblende-gabbros, amphibolites, diorites, microgranodiorites* and *microgranites*. The first members of this series, rich in augite, hornblende and basic plagioclases, conserved best their original textures owing to their resistance against the granitizing and anatectic agents. Further members of this series underwent more and more essential metasomatic transformations, became gradually impoverished in hornblende, which was substituted by biotite, and enriched in quartz and potash-feldspar; thus they approached evermore the granitic composition. Finally by a relaxation of their internal structure, they passed into diachytic types, dissolving and soaking in the surrounding red granites. The differentiation of that lipotectic series consists therefore in a varying grade of metasomatic granitization; finally, however, it interlocks with gradual granitic fusion, i.e., with true palingenesis.

In the light of those observations it seems justified to consider the granitic areas of North Volhynia as a scene of far advanced anatexis, in so far as considerable amounts of true granitic magma have been produced. This process was probably preceded by granitizing metasomatism, which may be conserved in various stages in the lipotectites. The rock-masses dissolved by anatexis seem to have been submitted to some process of differentiation, resembling closely that assumed by classic petrology for normal primary magmas (differentiation by fractional crystallization after Vogt, Bowen and others). Obviously, it would be hardly admissible, that amidst these palingenetic masses a gravitative crystal-settling could play any important rôle; yet it may be expected, that differential movements of these masses during orogenesis could squeeze out the intergranular liquid and separate to some extent various phases from each other.

The whole complex of differential processes during anatexis may be called *anatectic differentiation*. The resemblance of its effects with those of the differentiation of primary magmas is not difficult to explain, as has been pointed out long ago by Eskola. Fractional crystallization of the melt by a fall of temperature or by the escape of volatiles, and fractional fusion at rising temperature, or by an afflux of volatiles, are to some extent reversible processes; the action of both should lead, in their various stages, to similar, sometimes maybe identical results.

In the northern part of the Volhynian Archaean, as examined by the author, the process of anatexis reached probably a very high degree. The palingenites, comprising the series of red granites and allied rocks, make up over 90 per cent of the total area. Lipotectites, however, amount to less than 10 per cent and comprise chiefly dark rocks rich in hornblende and plagioclase, i.e., very refractory mineral combinations. This would mean, that the area in question originates from very deep zones of orogenesis. The graph 2a represents the differentiation of palingenites and lipotectites with regard to the following mineralogical parameters, calculated from micrometric analyses of rock-slides of 220 rock-samples (in vol. percentages):—

Q — quartz
A′ — alkali-feldspar (potash- and soda-feldspar)
P′ — plagioclase more calcic than 12 per cent of anorthite
A — alkali-feldspar without albite
P — plagioclase including separate albite
Σmaf — sum of mafic minerals
An — Percentage of anorthite in the plagioclase

The graph is composed of a triangle QA′ P′ (Q + A′ + P′ = 100) and of a twofold orthogonal diagram, illustrating the relation of Σmaf to P and of An to P. It may be seen here, that the lipotectites are more melanocratic and for the most part rich in plagioclase with higher anorthite-content. On the other hand, the palingenites extend in a wide belt from the alkali-types (on the side A′Q of

the triangle) far on the right, reaching the field of plagioclase-rocks, overlapping there partly the lipotectic area; in the lower part of the graph they manifest themselves as quite leucocratic (low Σmaf) and less calcic (lower An) than the lipotectites.

The southern part of the Volhynian Archaean, on the Slucz and Korczyk-rivers, exhibits a different lithological composition (Smulikowski, 1947). Most part of that area is composed of fine-granular gray gneisses, which are invaded in a synkinematic manner by light-gray granites and granodiorites of Korzec-type, or intricately migmatized by them. In some places they are intruded by discordant younger granites or tonalites. Reddish granites, comparable with palingenites of the northern part of Volhynia, outcrop there but locally in subordinate amounts, as posterior impregnations in mig-matitic rock-complex; they have been formed at its expense by way of metasomatic granitization


Lipotectites

Palingenites
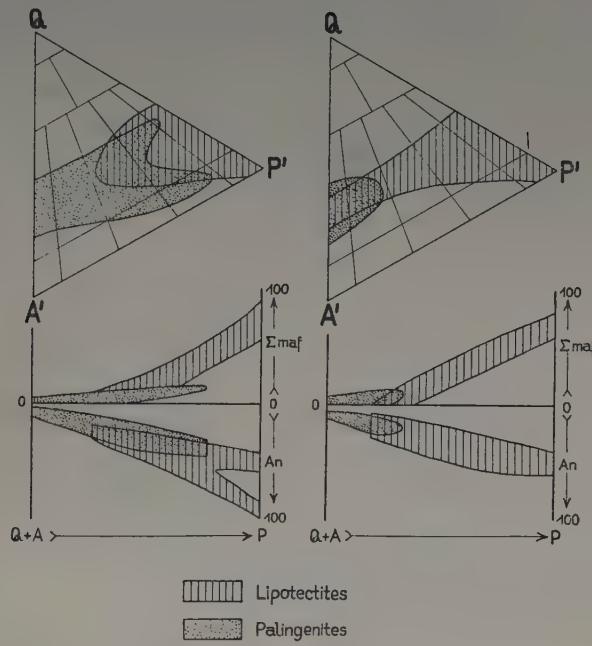
fig. 2a
Northern Part

fig. 2b
Southern Part

of the Granitic Areas of Volhynia

or by palingenesis on a very small and initial scale. It seems probable therefore, that we have here to do with a very shallow level of anatexis, which could affect the older gneisso-granitic complex in but an insignificant grade. According to such supposition the graph 2b shows the red palingenites strongly restricted to a small field at the side A'Q of the triangle, i.e., very little differentiated and holding but highly alkaline and potassic rocks from the initial stages of liquefaction. On the other hand the gray granito-gneissic (migmatitic) rocks, not affected by the transformation, extend far to the left from the plagioclase-corner of the triangle, filling the total range of differentiation.

A petrological comparison of both northern and southern parts of the Volhynian Archaean, as given by the graphs 2a and 2b, leads to the hypothesis that the older complex of gray granito-gneissic masses was the primitive substratum, which in later stages of the orogenic evolution was submitted to regional anatexis and furnished secondary red granites (palingenites). Northern areas present probably products of deeper levels emerging in a anticlinorial belt of mountain-chain (*Volhynides* after Malkowski); their presumed level of anatexis might be traced in the schematic graph Fig. 1 at a-a.

On the other hand the southern part of Volhynia might be considered as products of very shallow levels of anatexis, near its upper limit (b-b in the graph Fig. 1); this would mean, that they remain on the limbs of the Volhynides chain or within its synclinorial zone.

The conception of *anatectic differentiation* formed on the basis of long petrological studies in granitic areas of Volhynia ought to be quite important not only for petrology and tectonics of crystalline massifs. The possibility of multiple and repeated anatexis of older rock-masses during later phases and periods of orogenesis reveals very wide perspectives for the geochemistry of the sialic continental shields. It is the principal scope of the present report to call attention to such geochemical perspectives.

The distribution of chemical elements within the Earth's crust ought to be examined on the basis of a general cycle of its evolution. Such a cycle may be considered as beginning from true magmas of partly primary origin (" juvenile "). From the activity and different products of this magma it passes over the processes of weathering, transport and sedimentation, down to the metamorphism and further to the anatexis, producing new palingenetic melts and thus joining again with magmatic activity (general scheme Fig. 3). Each of these sectors of the cyclic evolution of the Earth's crust, has its own mode of differentiation, governing the geochemical migration and distribution of several elements. The geochemical behaviour of each element depends on its individual properties at different scales of physico-chemical conditions proper to various sectors of the cycle. The anatexis and the differentiation connected with it must play also a very important role in the geochemistry of the Earth's crust, as was pointed out by Eskola and Rankama.
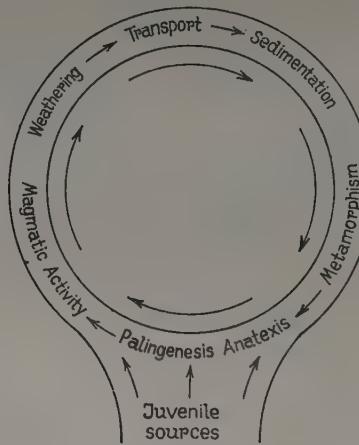

fig. 3

Evolutional Cycle of the Earth's Crust

Modern geochemistry considers the sialic Earth's crust (after Goldschmidt) as the place of concentration of various products of rest-crystallization; on the way of fractional crystallization of a basic primitive magma the last-crystallizing elements form a rest-magma usually of granitic composition, accumulating at the top of the silicate-zone of the Earth. In this way the sialic Earth-crust (called often " granitic layer ") was distinctly enriched in such elements as K, Li, Rb, Cs, Be, Sr, Ba, B, Rare Earths, Th, U, Nb, Ta, W, etc., but impoverished in Mg, Ca, Ti, Fe, Cr, V, P, Ni, etc. This fundamental thesis of geochemistry should be rejected nowadays, as modern petrologists affirm more and more often, that the granites do not originate from the differentiation-remnants of any basic primary magma, but are produced by a transformation of various, chiefly sedimentary, rocks. A metasomatic migration of several elements, during the granitization of sedimentary complexes, cannot explain the whole

problem of geo-chemical differentiation of all elements within the Earth's crust in such a complete and theoretically justified manner, as was done by Goldschmidt's hypothesis.

The introduction of the *anatectic differentiation* into general geochemical considerations could remove most of these troubles and generalize the principal idea of Goldschmidt. Because during the anatexis of older rock-complexes, consisting of sedimentary as well as igneous materials, the fractional fusion must introduce into palingenites first, all the elements of rest-crystallization and leave the elements of earlier crystallization in a non-mobilized state in the lipotectites. Thus the palingenites must be enriched in the elements of the former, and impoverished in elements of the latter group. During orogenesis the palingenites, as essentially fluid, are mobilized and conveyed in an upward direction more easily than the lipotectites. Thus in the course of the full history of the Earth's crust its uppermost layers must have been strongly enriched in acid leucocratic and alkali-rich rocks of granitic composition, concentrating all elements of rest-crystallization. The geochemistry of the Earth's crust seems therefore to manifest a very significant convergence: primary as well as secondary processes of differentiation lead to quite similar effects of accumulation of granites in the superficial layers of the Earth.
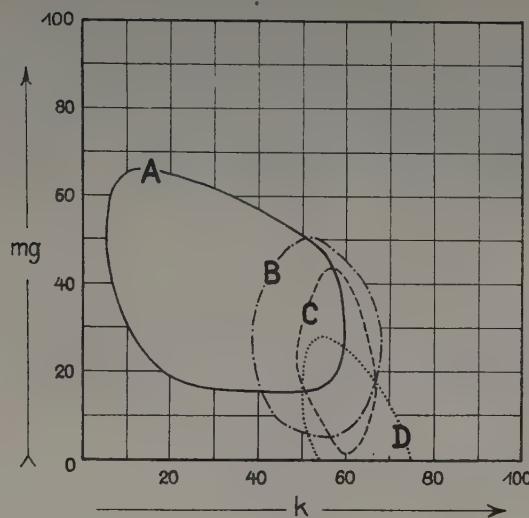

fig. 4

Niggli's Diagram of Finnish Granites

Such views in geochemistry were formulated for the first time by Rankama (1946). This author made a distinction between *granitophile elements*, which pass during anatexis into fluid fractions, and *granitophobe elements*, which remain in the infusible portions. If in an area many granitic intrusions of different age are found side by side, it may be supposed that the younger granites are at least in part products of palingenesis of the older ones. Selective fusion, repeated several times, would increase gradually the concentration of granitophile elements in the younger granites, as was in fact stated by Rankama, in some cases for several rare elements as Li, Rb, Cs, Be, Ba, Lanthanides, Ta and Pb. The conclusion of the writer drawn from his petrological studies of Volhynia, as concerning the geochemical importance of anatectic differentiation, harmonize very well with these geochemical data.

Finally an example from the Finnish Pre-Cambrian may be cited, supporting the thesis of anatectic differentiation. The crystalline trunk of the *Svecofennides* in Middle- and South-Finland contains four groups of granitic intrusion of different age: (A) *Prim-orogenic gray svecofennian granodiorites*, (B) *Ser-orogenic svecofennian granites*, (C) *Post-orogenic porphyroide granites* (Onas, Obbnas, etc.)

and (D) *Post-orogenic late-Precambrian granites of Rapakivi-type*. A petrologic comparison of the chemical composition of these four granite-groups shows some characteristic and consistent differences. The younger the granite-group, the richer it is at average in potash-feldspar, the poorer in plagioclase and especially in anorthite. The highest amounts of plagioclase occur in the oldest intrusions, which are commonly of granodioritic or tonalitic composition; the smallest content of plagioclase and the greatest content of potash-feldspar are found in the youngest Rapakivi-group. Both medial groups show an intermediate composition.

Such chemical relations may be demonstrated best in the square-diagram of Niggli, illustrating molecular proportions of potash to soda and of magnesia to iron (k/mg—Fig. 4). On the basis of chemical analyses the fields of distribution of each granite-group are drawn in this diagram. The following regularity may be then confirmed: the younger the rock-group, the higher the potash/soda and iron/magnesia ratio. At the same time the dispersion of rocks diminishes, denoting a growingly stronger selection of their chemical composition. These observations lead to a supposition, that the aforenamed granite-groups A-D were born successively one of another by differential anatexis, and owing to anatectic differentiation their chemical composition was specialized in the above-mentioned manner.

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ON THE PECULIAR FEATURES OF THE SEDIMENTARY ORE PROCESS IN THE GEOCHEMISTRY OF IRON

By N. M. STRAKHOV

U.S.S.R.

ABSTRACT

As shown by the distribution of iron in the sediments of a number of present water basins: Lake Balkhash, Aral Sea, Black Sea, Caspian Sea, Lake Issyk-kul, Atlantic Ocean, Barents Sea, Lake Baikal, the iron content of sands is the lowest, that of silts, higher, and that of clay sediments, the highest. In this way, as sediments, iron ores are not formed.

The distribution of iron in water basins is controlled by at least five independent processes: (1) supply of iron by rivers and its distribution in the water basin by water movements; (2) subaqueous seepage of ground waters; (3) deep current; (4) migration of iron during diagenesis; (5) subaqueous hydrothermæ.

Only the second, fourth, and fifth of the above processes are ore-forming, and to each of these a particular type of ore corresponds. With subaqueous seepage of ground waters, hematite, hematite-chamosite, chamosite, chamosite-bauxite ores of an oolitic texture are formed, occurring in beds of greater or lesser size. With diagenesis of fresh-water lake sediments, inland seas, and lagoons, concretional siderite ores are formed; the same are produced also in sediments of normal water basins low in carbonates. Subaqueous hydrothermæ produce hematitic (and possibly pyritic) ores, occurring in short but thick lenses; these ores are peculiar to geosynclinal zones.

CONCENTRATION AND DISSEMINATION OF CHEMICAL ELEMENTS IN THE EARTH'S CRUST AS A RESULT OF OXIDATION AND REDUCTION PROCESSES

By V. TSCHERBINA

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ABSTRACT

1. The following 33 elements take part in the oxidation-reduction reactions of the earth's crust (i.e., one-third of all the elements of the periodic system): H, C, N, O, P, S, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, As, Se, Mo, Ru, Pd, Ag, Sn, Sb, Te, I, Ce, W, Re, Os, Pt, Au, Hg, Pb, Bi, U.

2. The elements concentrated upon oxidation are generally disseminated upon reduction, and vice versa.

3. The following are concentrated as a result of oxidation:
    (a) Elements forming oxidized, easily hydrolyzed compounds with a precipitation of slightly soluble hydroxides: Fe (OH_3), MnO_2, Co_2O_3, PbO_2, Ce $(OH)_4$.
    (b) Salts of metallic acids: MoO_4'', VO_4''', CrO_4'', etc., as well as PO_4''' and AsO_4''', partly SO_4'', SeO_3'', FeO_3'', giving difficultly soluble salts with Ca, Pb, Fe''' and some other cations.
    (c) Compounds that are less volatile in the oxidized form than their free elements; for H, N, S, Hg these are water, hydro-carbons, nitrates, sulphates, cinnabar.

4. The following are concentrated as a result of reduction:
    (a) Native metals formed upon reduction of their oxides (excepting mercury) and carbon.
    (b) Some oxides: Cu_2O, MoO_2, ReO_2, UO_2, as well as HgCl.
    (c) S, Se, Te in combinations with metals of the type of sulphides.

5. The direction of the oxidation-reduction processes is determined by the facies in which they occur.

THE DISTRIBUTION OF Cr, V, Ni, Co AND Cu DURING THE FRACTIONAL CRYSTALLIZATION OF A BASIC MAGMA

By L. R. WAGER and R. L. MITCHELL

Great Britain

ABSTRACT

The amounts of certain trace elements have been determined by optical spectrographic methods in minerals separated from the Skaergaard intrusion. The minerals were formed successively as a primary precipitate from a convecting mass of basic magma (Wager and Deer, *Meddel. om Grönland*, Band 105, No. 4, 1939). The amounts of trace elements in the original magma have been obtained from analysis of the chilled marginal gabbro and sufficient later rocks have been analyzed to allow estimates to be made of the trace element composition of successive residual magmas. By comparing the amounts of the trace elements in the crystal phases and the amounts in the corresponding magma an approximate distribution ratio between liquid and crystal phases has been obtained.

In the case of Cr, Ni, and Co the amounts precipitated in chromite and in early pyroxenes and olivines are greater than the amounts in the magma. Thus the amounts of these elements in successive residual magmas decline—Cr and Ni rapidly, and Co slowly. On the other hand the amounts of V and Cu precipitated in the early minerals are less than the amounts of these elements in the original magma, and the amounts of these elements increase for a time in successive residual magmas and then also decline rapidly. In the later rocks Cu enters with about equal ease into the feldspar, pyroxene, olivine, and iron ores; so far no convincing crystal chemical explanation of this has been found.

The trace element composition of the iron ores has been investigated; early primary precipitates of iron ores have a trace element composition comparable with average values for titaniferous iron ores as found by Landergren (*Sveriges Geologiska Undersokning*, Arsbok 42 (1948) No. 5), while later iron ores have a composition comparable with Landergren's average values for the apatite iron ores.

I. INTRODUCTION

THIS communication deals with the distribution of certain trace elements in the layered Skaergaard intrusion of East Greenland. As Buddington (1943) has emphasized, the detailed study of layered intrusions should provide data of special significance for geochemical problems.

The broad factors controlling the distribution of trace elements have been magnificently elucidated by V. M. Goldschmidt and his collaborators. Their generalizations were based on determinations of trace constituents in rocks and minerals of all kinds of paragenesis and from localities widely scattered about the world. The data here presented, like those of Nockolds and Mitchell given in their recent paper on the geochemistry of some Caledonian plutonic rocks (1948), are the results of analyses of a series of related rocks and of the rock-forming minerals separated from them. A stage has now been reached when, in our view, investigations are urgently required of the trace elements in the rocks and the individual rock-forming minerals of single intrusion complexes or of single petrographic provinces where the petrogenesis is reasonably well understood.

Goldschmidt's geochemical work led to an understanding of what may be called the crystal-chemical factors of trace element distribution such as ionic size, charge and polarization, and it will be seen that these factors are operative in the rocks and minerals here considered. But besides the crystal-chemical factors there are geological or petrogenetic factors which exercise a different, but equally important control. In the case of the Skaergaard intrusion, the main petrogenetic process involved in the distribution of both the major and minor constituents was fractional crystallization.

The petrology of the Skaergaard intrusion has already been described in some detail (Wager and

Deer, 1939). The intrusion was originally a pool of basaltic magma within the upper crust, having a volume of about 300 cu. km. The initial composition, judged by the nature of the chilled phase at contacts, was that of a fairly typical olivine basalt. During cooling strong fractionation took place, giving the layered series which is several kilometres thick and which was built up from the bottom upwards, by the accumulation of crystals successively separated from the overlying liquid. It is estimated that half the layered series is at present inaccessible, being beneath the present level of
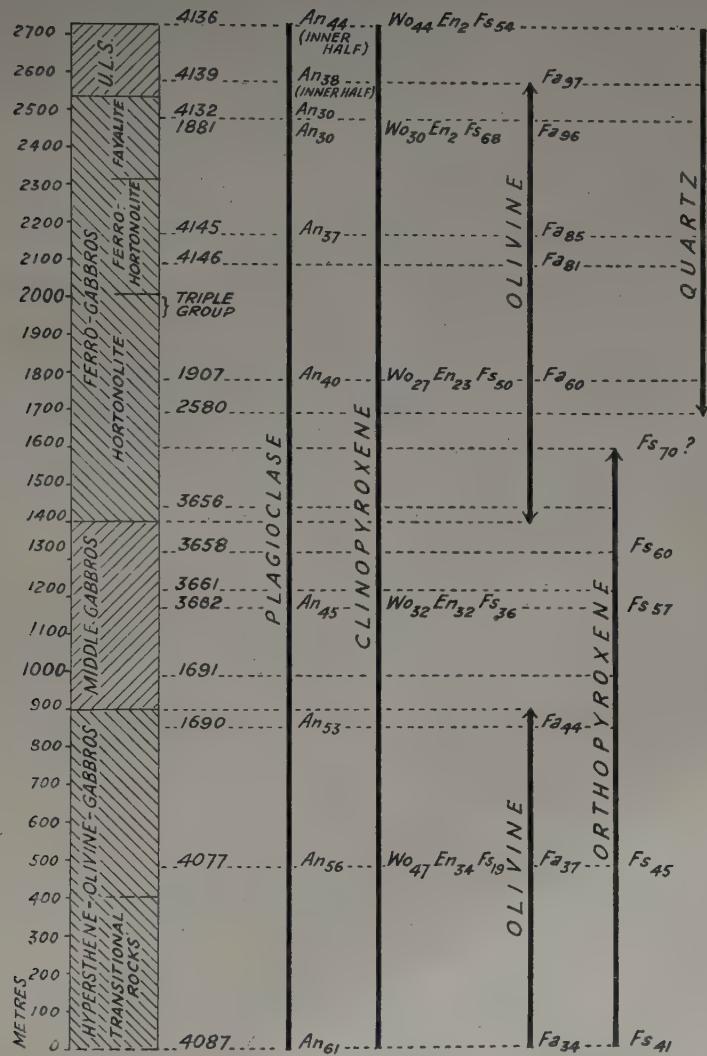
FIG. 1.—*Composition of the chief minerals of the layered series plotted against height in the intrusion. (Reproduced by permission from Meddel. om Grönland, Bd. 105, 1939).*

erosion. The chief minerals in the accessible layered rocks and their changes of composition are shown diagrammatically in Fig. 1.

The five trace elements to be considered summarily in this communication suffice to illustrate certain general principles. Data for several other trace elements have also been obtained and it is

TABLE I

Trace elements in Typical Rocks of the Skaergaard Intrusion arranged in Order of Solidification, and Comparisons
(Contents in p.p.m.)

	Ionic radius A	S	A Gabbro picrite	B Eucrite	C Olivine gabbro	D Middle gabbro	E Horton-olite ferro-gabbro	F Fayalite ferro-gabbro	G Basic Heden-bergite grano-phyre	H Acid grano-phyre	Z Marginal gabbro
(Al··· ...	0·57)										
Cr··· ...	0·64	1	1,500	300	230	—	—	1	—	14	170
(Ti·· ...	0·64)										
V·· ...	0·65	5	120	180	220	400	13	—	—	18	140
(Fe··· ...	0·67)										
Ni·· ...	0·78	2	1,000	350	120	40	—	—	4	8	170
(Mg·· ...	0·78)										
Co·· ...	0·82	2	90	80	48	40	30	7	12	5	53
...											
Cu·· ...	c. 0·8	10	100	50	67	180	350	300	500	20	130
(Fe·· ...	0·83)										

Garabal Hill—Glen Fyne Complex (Nockolds and Mitchell, 1948)

	Ultrabasic	Basic	Intermediate	Acid	
Cr...........................	2,500	300	150	60	
V	100	150	100	80	
Ni...........................	700	200	80	20	
Co...........................	200	70	30	15	

Averages as Oxides based on composite rock samples (Goldschmidt, 1937)

	Ultrabasic	Basic	Intermediate	Acid	
Cr_2O_3	5,000	500	100	3	
NiO	4,000	200	50	3	
CoO........................	300	100	40	10	

Notes for upper part of table (numbers refer to specimens described in Wager and Deer, 1939):

S ...... Spectrographic sensitivity in parts per million. A dash in the table indicates a content below this value.
A ...... Average for gabbro picrites 1,683 and 1,676.
B ...... Average for eucrites 1,851 and 1,846.
C ...... Average of three determinations of hypersthene olivine gabbro 4,077.
D ...... Average of middle gabbro 3,661 and 3,662 (olivine-free gabbro).
E ...... Average of hortonolite ferrogabbros 1,907 and 3,649.
F ...... Average of fayalite ferrogabbros 1,974, 4,142, and 1,906.
G ...... Average of basic hedenbergite granophyres 4,137 and 1,905.
H ...... Average of acid granophyres 3,058, 360, 359, 2,562, 4,064, 3,659.
Z ...... Average of chilled marginal gabbros 1,825, 1,724, 1,922 (taken to represent the composition of original Skaergaard magma).

Lower part of table:

The data for the Garabal Hill-Glen Fyne Complex are averages calculated from values given by Nockolds and Mitchell (1948, Table II, p. 338).

The data due to Goldschmidt are taken from his lecture to the Chemical Society (1937, p. 662).

proposed to present a full discussion elsewhere. The values for the amounts of the trace constituents in the rocks are the average of two or more separate determinations. The corresponding figures for individual minerals are the result of only one set of determinations, made on 0·02 gram of mineral grains, hand-picked from the crushed rocks. The spectrographic determinations have been carried out by one of us (R.L.M.) at the Macaulay Institute for Soil Research; the techniques used have been described elsewhere (Mitchell, 1940, 1948). It should be mentioned that spectrographic determinations of the minerals were made as particular hand-picked samples became available, and that any general trend of the data for particular minerals only became evident when the data were finally assembled. The figures presented are considered to be between half and twice the true value, but we shall not in this place discuss the evidence for this. Much of the interest of the present data is comparative and does not depend on the absolute values for the different constituents. With increase in the number of spectrographic determinations there is some increase in accuracy. This we have indicated by giving two significant figures in the tables, but by this we do not wish to imply that the values are correct to two significant figures. Preliminary data for the Skaergaard rocks have previously been presented (Wager and Mitchell, 1943). The same general trend is shown by our present data but, where the actual values differ, the present figures are regarded as the more satisfactory. Data for the minerals separated from the rocks have so far not been presented except for certain pyroxenes and olivines (Wager and Mitchell, 1945).

II. DATA FOR THE ROCKS

The data for the rocks are given in the first part of Table I. The gabbro picrites and eucrites of columns A and B are early fractions found in the border group. They are regarded as roughly equivalent to rocks of the lower part of the layered series which are below the limit of present day observation. The rocks of columns C to G represent average rocks of the layered series in ascending order, and this is also the order of solidification. Rocks of column H are the latest of the complex and are considered to be fractions produced by filter press action in the later stages of the cooling. Column Z is the average of four chilled marginal gabbros and is considered to represent the composition of the original magma.

Looked at broadly, the results for this series of rocks are what would be expected from the early work of Goldschmidt and others. Thus there is a concentration of chromium and nickel in the early rocks; slight concentration of cobalt in the early rocks and much less complete reduction in the amount of this element in the later rocks compared with Cr and Ni; and concentration of vanadium and copper in the middle, or later middle parts of the series. In the lower part of Table I comparison is made with Goldschmidt's data for average ultrabasic, basic, intermediate and acid rocks for the three elements for which data are available. Average data are also given for the Garabal Hill-Glen Fyne complex. The same general trend in the amounts of chromium, cobalt and nickel, as in the Skaergaard intrusion, is seen in these examples but there are divergencies in the case of the intermediate rocks. Thus under conditions of strong fractionation like that giving the Skaergaard complex, there is a much more complete elimination of chromium and nickel in the intermediate rocks. Indeed this almost complete elimination of certain elements under strong fractionation is a remarkable and unexpected feature. Somewhat similar trends have been found among a rather complicated series of rocks in Roslagen, Sweden, by Lundegårdh (1946).

III. DATA FOR THE MINERALS

Data for the minerals are assembled in Table II. Only minerals regarded as having been a primary precipitate of crystals from the convecting magma pool, were separated for analysis. These crystals are essentially unzoned except for an intermittent and narrow fringe of lower temperature solid solutions which crystallized from the magma present in the interstices of the primary precipitate.

PART II: PROBLEMS OF GEOCHEMISTRY

TABLE II

Trace Elements in Minerals separated from Rocks of the Skaergaard Intrusion compared with the Amounts in the Corresponding Rocks and the Estimated Amounts in the Corresponding Liquids

(Contents in p.p.m.)

		A Gabbro picrite	B Eucrite	C Olivine gabbro	D Middle gabbro	E Horton-olite ferro-gabbro	F Fayalite ferro-gabbro	G Basic heden-bergite grano-phyre	H Acid grano-phyre
Cr (S=1)	Rock	1,500	300	230	—	—	1	—	14
	Plagioclase		10	—	—	—	—		
	Pyroxene		3,000	350	—	—	—		
	Olivine		20(?)	—	No ol.	—	—		
	Ilmenite			2	—	—	—		
	Magnetite			200	—	—	—	—	
	Liquid (estimated)	170		70		¾	1½	5	15
V (S=5)	Rock	120	180	220	400	13	—	—	18
	Plagioclase		10	—	10	10	—		
	Pyroxene		300	250	100	30	—		
	Olivine		—	—	No ol.	—	—		
	Ilmenite			600	300	20	—		
	Magnetite			2,000	800	300	—		
	Liquid (estimated)	140		230		10	1	4	18
Ni (S=2)	Rock	1,000	350	120	40	—	—	4	8
	Plagioclase		10	—	—	—	—		
	Pyroxene		200	140	50	—	—		
	Olivine		2,000	325	No ol.	10	—		
	Ilmenite			150	50				
	Magnetite			300	100				
	Liquid (estimated)	170		60		½	1½	5	8
Co (S=2)	Rock	90	80	48	40	30	7	12	5
	Plagioclase		—	—	—	—	—		
	Pyroxene		60	50	60	40	15		
	Olivine		150	125	No ol.	100	20		
	Ilmenite			80	100	70 30			
	Magnetite			80	80	60 30	3		
	Liquid (estimated)	55		40		20	13	5	5
Cu (S=10)	Rock	100	50	67	180	350	300	500	20
	Plagioclase		15	35	15	250 700	10		
	Pyroxene		—	35	100	300 1,000	100		
	Olivine		20	20	No ol.	300 400	20		
	Ilmenite			100	30	300 400			
	Magnetite			20	50	500 300	400(?)		
	Liquid (estimated)	130		200		350	450	250	20

Notes: The minerals were separated from one or other of the rocks mentioned in the explanation to Table I except in certain cases where the figures are written across the column when the mineral was separated from some intermediate rock. This is particularly the case with the iron ores which are not present as a primary precipitate in the typical olivine gabbro (column C) but only in a gabbro transitional to the olivine-free gabbros (column D). A question mark in brackets (?) is placed when contamination of the hand-picked mineral by some other mineral present in the rock is suspected to have influenced the figures quoted. S indicates the spectrographic sensitivity in parts per million. A dash in the table indicates a content below this value.

In the table are also given (1) the amounts of the various trace elements in the rocks from which the mineral grains were obtained and (2) an estimate of the amounts in the successive residual liquids from which the minerals were precipitated. The latter estimation is possible because the Skaergaard intrusion forms a closed system in which the volume, initial composition, and sequence of the various rock types is tolerably well known. The amounts of the trace constituents in the residual liquids have been estimated at the same stages in the cooling as has already been done for the major constituents (Wager and Deer, 1939, p. 217).

Since an approximation can be obtained to the composition of the liquid from which the minerals of the primary precipitate were separating, and since the composition of the crystals themselves is known, an idea of the distribution factor between crystal and liquid phases may be obtained. In dealing with trace constituents this concept of a distribution factor has in general only been applied in qualitative terms such, for instance, as saying that chromium enters preferentially into pyroxenes rather than olivines. It is clearly desirable when possible, to express this degree of preference more definitely and our data allow, in some cases, a semi-qualitative value to be given for the approximate distribution factor between liquid and certain crystal phases.

The data presented in Table II may conveniently be discussed for each element separately, beginning with chromium. Under column A no data are given for minerals because satisfactorily pure minerals have not been separated from the gabbro picrites. The olivine, present in fairly large crystals in the gabbro picrite, contains small opaque inclusions often showing crystal shape. This olivine with its inclusions was analyzed spectrographically and the considerable amount of chromium found is considered to be in the opaque inclusions which are interpreted as chromite. It appears that chromite was precipitated from the Skaergaard magma although there was only $0 \cdot 02$ per cent Cr_2O_3 in the magma. The extreme insolubility of chromite in basic magma was pointed out many years ago by Vogt (1921, p. 322). From the eucrite, which is also an early rock, plagioclase, pyroxene and olivine were separated and analyzed. Chromium largely enters the pyroxene and there is little or none in the plagioclase and olivine. This is no doubt to be correlated with the existence of chromian pyroxenes, while chromian varieties of olivine and plagioclase have not been described. Spectrographic analysis shows 10 p.p.m. of chromium in the plagioclase separated from this rock. Contamination of the analyzed plagioclase sample by one part in a thousand of pyroxene would account for this small amount of chromium but it is considered more likely that the chromium shown is actually present in the crystal lattice of the plagioclase. The olivine sample may have been more heavily contaminated because of the greater similarity in appearance of olivine and pyroxene. The 20 p.p.m. of chromium in this olivine is thought to be due mainly to contamination of the olivine by pyroxene to the extent of one part in 300.

The pyroxene of the eucrite has 17 per cent of the ferrosilite molecule (Wager and Deer, 1939, p. 152) and 3,000 p.p.m. Cr; the pyroxene of the olivine gabbro contains 19 per cent Fs. (Wager and Deer, 1939, pp. 77-8), and 350 p.p.m. Cr; and the pyroxene of the middle gabbro contains 36 per cent Fs. and < 1 p.p.m. Cr. The changes taking place in certain trace constituents are more violent than the changes in the major constituents and the virtually complete absence of Cr from the three later pyroxenes which have been separated is surprising.

After the early precipitation of chromite in very small quantities there was a period of fractionation during which no spinel mineral formed as a primary precipitate. At a later stage, namely between the formation of the olivine gabbro and the middle gabbro, magnetite and ilmenite both became primary precipitates. By this stage there is little chromium left in the magma and what there is enters the magnetite and not the ilmenite. The separation of the analyzed samples of the ore minerals was made by a rough magnetic method and it was considered that it would only provide samples considerably contaminated one by the other. Taking this into consideration it is clear that the ilmenite is essentially free from chromium while the magnetite contains 200 p.p.m. The chromium in the magnetite is presumably replacing $Fe \cdots$ and it apparently is not able to enter the ilmenite structure so readily. Had the original magma been more oxidized, magnetite would no doubt have appeared earlier in the

fractional crystallization process and the magnetite would have been richer in chromium, because at that time, there would have been more chromium available in the magma to enter it. Such conditions seem to have occurred in the Bushveld and other complexes where magnetites contain considerable amounts of Cr. The iron ores separated from the rocks of the middle and upper parts of the layered series are virtually free from chromium. Further consideration is given to the iron ores below.

The chromium distribution factor between pyroxene and liquid for the early rocks (column B) is 20 : 1; for the next pyroxene analyzed (column C) it is 5 : 1, and for the olivine in this same rock (column C) the distribution factor between crystal and liquid is 1 : > 70. These figures give a measure of how much more readily the chromium ion enters the pyroxene than the olivine structure.

The amounts of chromium in the original liquid and the estimated amounts in successive residual magmas show a steady decline until the upper part of the layered series where the magma has become granitic in composition. At this stage our data show a slight increase in Cr. Chromium enters early-separating crystal phases with such facility that the amount in the residual liquid is at certain stages reduced below 1 p.p.m.

The distribution of vanadium may next be considered. Vanadium is present in moderate amounts in the early rocks, reaches a maximum about the middle of the series and then falls to very low amounts. The figures of columns B and C, show that the bulk of the V in the rock is present in pyroxene, where it is no doubt replacing ferric iron. When ilmenite and magnetite become primary precipitates, between the stages C and D, V enters abundantly into both of these minerals. In the case of magnetite the V is again presumably replacing ferric iron. Vanadium magnetites or maghemites have been described, particularly from India (Dunn and Dey, 1937). Our data show that a significant amount of V is present in ilmenite and the question arises as to whether V is there replacing Ti. In the four olivines investigated the amount of V is below the sensitivity, that is below 5 p.p.m. On the other hand some of the plagioclases investigated contained 10 or 15 p.p.m. of vanadium. We do not regard the V in the plagioclase as due to contamination with fragments of pyroxene or iron ore, as such contamination would be far more likely to occur in the olivine samples, but instead we believe that vanadium is present in some of the plagioclases in significant amounts. Its presence is comparable with that of ferric iron which from recent analyses by W. A. Deer (data not yet published) is seen to be a significant constituent of plagioclases separated from the Skaergaard intrusion. The plagioclase separated from the olivine gabbro, column C, is given as having less V than the sensitivity. Re-examination of the spectrograms suggests that the figure is really round about the sensitivity, i.e., 5 p.p.m., but in this case, as in others, we have not revised the first reading of the plates. The reduction of V below the sensitivity is no doubt a real effect in the case of the plagioclase of the fayalite ferro-gabbro as at this stage there was so little in the magma.

The estimated amounts of V in the successive liquids show a rise before falling away later to low figures of about 1 p.p.m. The total amounts of V separating in the early minerals was less than that present in the original liquid. Thus during the early stages of fractionation there was some enrichment of V in the residual liquid. Later, when ilmenite and magnetite became primary precipitates they received so much V from the liquid that the amount in the liquid fell rapidly. In the granophyric liquids (columns G and H) there is estimated to be a slight increase in the amount of V as for Cr.

Nickel and cobalt may conveniently be considered together. Ni is strongly concentrated in the early rocks while Co is more evenly spread throughout the series. Both elements are present in pyroxene, olivine and iron ores. The Ni and Co occupy the Mg-Fe positions in the structures. According to Goldschmidt (see for instance 1945, pp. 3-4) Ni enters more readily than Mg because of the polarization of the Ni ion. This view is supported by the data presented here. The amount of Ni in pyroxene at stage E is less than the sensitivity (i.e. < 2 p.p.m.), while in this rock the pyroxene still contains 8·33 per cent MgO. Co remains abundant in the middle of the ferro-magnesian series and this is ascribed to the ionic size of Co being but little less than that of ferrous iron.

In comparing pyroxene and olivine from the same rock it is clear that Ni and Co are both more abundant in olivine than pyroxene. This is apparently due to the greater amount of Mg and Fe in the olivines than in the pyroxenes, which means that there is more opportunity for replacement in the olivines than the pyroxenes. The early iron ores, formed between stages C and D, contain about twice as much Ni as Co. In the later iron ores the proportions are reversed and, indeed, iron ores of stage E have < 2 p.p.m. of Ni while they contain 60 p.p.m. of Co. In the latest magnetite separated, column F, the amount of cobalt has finally fallen to only 3 p.p.m. Lundegardh (1946, pp. 150-51) has pointed out the change in the ratio of Ni to Co in rock series produced by differentiation.

The estimated composition of the various residual liquids shows a rapid decline in the amount of Ni to a very low figure. There is then a slight increase in the amount of nickel, similar to that shown by chromium and vanadium. The amount of cobalt in the successive residual liquids shows a gentle decline throughout.

The last element to be considered is copper, which is strikingly more abundant in the rocks of the later middle part of the series than in either the early or latest rocks. At all the stages in the differentiation series copper shows a tendency to be present about equally in all the minerals considered. Thus in plagioclase, pyroxene, olivine and iron ores the amount of copper increases on the whole until the hortonolite ferrogabbro, and ferrohortonolite ferrogabbro stages are reached when all five minerals contain about 300-1000 p.p.m. After this there is a marked decline in the copper content of the plagioclase, pyroxene and olivine, while in the magnetite it remains moderately high. It is probable that copper replaces iron in the ferro-magnesian minerals and that it can replace sodium at certain stages in the plagioclase solid solution series.* Goldschmidt has described the copper ion as " sausage shaped " (verbal communication) implying that it tends to be able to fit itself into various shaped spaces in the crystal structure providing they are reasonably near the right size.

Because relatively little copper is precipitated in the early minerals the amount of copper in the successive residual magmas increases considerably, from 130 p.p.m. to about 450 p.p.m. at the fayalite ferrogabbro stage. In the latest liquid of acid granophyre composition the amount has fallen to 20 p.p.m.

The data for the Skaergaard magnetites are compared with other available data in Table III. The Bushveld iron ores and titaniferous iron ores analyzed by Landergren are richer in Cr and Ni than the earliest Skaergaard magnetite. Had magnetite separated earlier from the Skaergaard magma, when there was more Cr and Ni present in the magma, then it is to be expected that this magnetite would have resembled in a general way the Bushveld magnetites and Landergren's average for titaniferous iron ores. As suggested above, precipitation of magnetite would no doubt have occurred earlier in the Skaergaard complex if the magma had been in a less reduced condition. The apatite iron ores of Kiruna are poor in Cr and are comparable with iron ores of the Skaergaard intrusion from the Middle Gabbros (column D). Shortly after the Middle Gabbro stage in the Skaergaard differentiation, apatite became a primary precipitate. The Skaergaard data suggest that apatite iron ores may belong to a later stage of fractional crystallization-differentiation than the typical titaniferous iron ores. Analyses of two late magnetites from acid pegmatites in Central Sweden made by Lundegardh (1946) have very little Cr, Ni and Co and are thus comparable with the late Skaergaard magnetites. Data for the unusual magnetite from Katmai given by Zies (1938) are also of interest especially for the Cu and Mo content.

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*Since this communication was read a renewed attempt has been made to find an explanation of the peculiarities in the distribution of copper. The fact that the copper content of the fayalite ferrogabbro is high (see column F, Table I) while the contents of the separated minerals from this rock are small (see bottom of Table II) suggested the presence of some copper mineral. Examination of polished specimens of the fayalite ferrogabbro shows the presence of sulphide minerals, and the textural features suggest that, at an early stage, an immiscible, liquid sulphide phase formed as droplets in the silicate melt. It appears that the copper in the magma largely entered the sulphide liquid, depleting the silicate magma in this element. Thus the plagioclase, pyroxene, olivine, and iron ores which separated from the silicate part of the magma contain only low amounts of copper.

TABLE III

Iron Ores from the Skaergaard Intrusion and other sources

(Contents in p.p.m.)

| | Bushveld magnetites | Titani-ferous iron ores (N. Sweden) | Skaergaard magnetites | | | | | Apatite iron ores (N. Sweden) | Late magnetite from pegmatites (Sweden) | Magnetite from Katmai |
| | | | Early | | | | Late | | | |
	1	2	CD	D	E	EF	F	3	4	5
Cr.........	2,800	2,200	200	—	—	—	—	<10	—	
V	1,800	1,400	2,000	800	300	—	—	1,300	100	
Mo		50	5	3	3	3	3	30		400
Ni...........	800	300	300	100	—	—	—	200	—	100
Co		200	80	80	60	30	3	90	—	200
Cu			20	50	500	300	400			2,300
Zn...........			Between 300 and 3,000							4,700

Notes:—

Column 1. Mean of first seven analyses of Bushveld magnetite ores (Hall, 1932, Table XLII, p. 346). These trace constituents have not been estimated in all the five analyses.

Column 2. Average values for titaniferous iron ores of North Sweden (Landergren, 1948, p. 108).

The Skaergaard data are the same as Table II with additions. The same letters are used for the columns as in the previous tables.

Column 3. Average values for apatite iron ores of North Sweden (Landergren, 1948, p. 108).

Column 4. Mean for two magnetites from acid pegmatites in Sweden (Lundegardh, 1946, p. 125 and p. 140).

Column 5. Magnetite of unusual origin and composition from Katmai, Alaska (Zies, 1938, pp. 385–404).

IV. CONCLUSION

The main intention of this paper is to show, by means of the tables of data, the actual trend in the amounts of trace constituents in a series of minerals formed by strong crystal fractionation. So far as can be seen this trend is in harmony with the crystal chemical factors of ionic size, charge, etc., brought to the notice of geologists by V.M. Goldschmidt. Crystal chemists may find in the new data some evidence for further consideration of these factors.

In addition, other general conclusions may be briefly indicated:—

(1) Under conditions of strong fractionation there may be striking variations in the amounts of trace constituents present in a mineral series. The changes in the proportions may be much more marked than the changes in the proportions of the major constituents. It is not wished to suggest that the trend shown by our data is the only trend likely to be shown by solid-solution series of minerals formed during fractional crystallization of basic magma, but it is suggested that it indicates the kind of variations to be expected under such conditions.

(2) The trace constituent composition of the minerals of igneous rocks is controlled by two different sets of factors. There are the crystal chemical factors such as ionic size and charge. These decide whether it is possible or not for the trace element to enter a particular crystal lattice. Whether the trace element actually does enter into the make-up of a particular crystal phase is controlled by a further set of factors which may be grouped under the heading of geological or petrogenetic factors. One of the most important of these is whether or not the sequence of events has been such that the trace element is available in the magma at the time of crystallization of a particular mineral. This may seem a self-evident point but it is nevertheless worth stating, and worth illustrating by reference to the iron ores (Table III). The early Skaergaard magnetites contain Cr, V and Ni in considerable

amounts while the later do not. There is no crystal-chemical reason why the ions of Cr, V and Ni should not enter the crystal structure of the later magnetites and the reason they are not present is that they are not available in the magma during the later stages of solidification. This is a matter of the petrogenetic history of the rocks.

(3) Crystal fractionation is seen to lead to an almost complete elimination of Cr, V and Ni in the residual magmas of the late middle stages, but it appears that in the final stage there is some slight increase in concentration of these. The cause of this is not clear but the state of oxidation of the element may be a factor in some cases.

(4) There is a rough relationship between the distribution of the trace elements at various stages in the differentiation of the Skaergaard magma and the usual associations shown by the mineral deposits of these elements. Thus mineral deposits of Cr and Ni are usually associated with ultrabasic or basic rocks while Cu tends to occur in association with basic and intermediate rocks; the same associations are found for these elements in the Skaergaard intrusion complex. The odd increase of Cr, V and Ni in the acid granophyre stage after the almost complete elimination at an earlier stage may possibly have some connection with the occasional occurrence of these elements as late oxidized ores.

(5) When the trace constituents of the intermediate rocks of the Skaergaard intrusion (Table I, columns E and F) are considered there is no reasonable correspondence with Goldschmidt's average for intermediate rocks or with the data for intermediate rocks from the Garabal Hill-Glen Fyne Complex (lower part of Table I). Typical intermediate rocks have not been formed by the strong fractional crystallization of the Skaergaard magma and this is true whether major or trace constituents are considered. (For the major constituents compare Wager and Deer, 1939, pp. 313-14 and Fig. 62). This may result from peculiarities in composition of the original Skaergaard magma or it may be due, as we have formerly suggested when considering the major constituents, to the bulk of the intermediate rocks in the Earth's crust having another origin than that of straightforward fractional crystallization (Wager and Deer, 1939, p. 324).

A possible alternative hypothesis to fractional crystallization for the origin of the intermediate rocks is that they result from mixing of basic and acid rocks. It is worth pointing out that, for the trace constituents here considered, mixing of basic rock (column C) with acid rock (column H) would give values for Cr, Ni and Co in accord with those found by Goldschmidt for the intermediate rocks. Thus, if the Skaergaard intrusion gives any indication of the way in which fractional crystallization of basalt normally takes place, then anything approaching typical intermediate rock would only be produced by mixing of the basic and acid differentiates, and this is true not only for the major constituents but also for the trace constituents here considered.

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PART II: PROBLEMS OF GEOCHEMISTRY

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THE VERTICAL CIRCULATION OF MATTER IN THE EARTH'S CRUST

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ABSTRACT

The paper deals with the vertical circulation brought about by isostatic adjustment and orogenic warping down of portions of the crust, whereby at certain depths the early melting alkaline feldspars are remelted and together with the volatiles, dissolve quartz and a little of the femic components furnishing palingenic granite magma. Since this granite magma is less dense than the remaining femic material of the partly molten rock, the granite magma will rise, forming an upper " sial " layer, the remaining femic material of the rocks forming the upper portion of the " sima " layer.

At certain depths the sodium-rich portions of the plaglioclases of diorites and gabbros will melt and together with the kaliophilite constituent of broken-up mica form foyaitic-phonolitic magmas. At places where the entire rockground is remelted we obtain the granodioritic magmas of the orogen plutons and andesite volcanoes accompanying orogenic movement. At a certain depth hornblende and mica break down and the excess of volatiles will, at temperatures above their critical one, dissolve fairly large amounts of iron and magnesia compounds forming juices, which on reaching higher levels of the earth's crust, bring about the " magnesiametasomatism " and related metamorphic processes. The cycle of vertical circulation is completed by the magmas rising from the sial and sima layers to the surface of the earth.

[Published in full as " Isostasy and the origin of sial and sima and of parental rock magmas " in *American Journal of Science*, vol. ccxlvii, 1949, pp. 145–167.]

DISCUSSION

P. NIGGLI said he would like to have the opinion of Prof. Wahl on two questions: (1) Does he think that the main part of the remelted earth shell belongs to sima or to old sedimentary rocks of the sial? (2) Have we an increase of the sialic continental layers in geological time?

He thought also that the first lavas in geosynclines are to a large part not spilitic lavas but normal basaltic ones.

W. WAHL (in reply): The thickness of the sial layer would depend on the temperature gradient, since a temperature level constitutes the lower temperature boundary surface of the sial. The thickness of the sial would thus vary with the geothermic gradient and be different under continental areas and orogenic belts, as it is from earthquake measurements actually known to be. As to the thickness of the salsima and the outer shells of the sima these would also on the same grounds, vary in different parts of the surface of the earth. The sima shell in its lower peridotitic parts would probably be of very great thickness.

Also the magmas originating in cratogenic regions are dealt with in the paper to be published. The differentiation of parental magmas is thought to take place principally during the ascent of the magmas from the shells in which they were produced into the upper parts of the earth crust.

DATE DUE

LIST OF THE PARTS OF THE REPORT OF THE EIGHTEENTH SESSION